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# Temperature-jump Studies of the Complex Formation of Nickel(II) L-Glutamate in Aqueous Solutions

Kiyoshi TAMURA,* Shoji HARADA,† Yoshinori FUNAKI,† and Tatsuya YASUNAGA†

*Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239*

*†Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730*

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Temperature-jump relaxation studies have been carried out on aqueous nickel(II)–L-glutamic acid solutions. The observed relaxation phenomenon is ascribed to the successive complex formation reactions:

$$Ni^{2+} + L^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiL,$$

$$NiL + L^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NiL_2^{2-},$$

$$NiL_2^{2-} + L^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiL_3^{4-},$$

where $L^{2-}$ denotes a glutamate ion. The rate constants are: $2.0\times10^4$, $1.1\times10^4$, and $9.2\times10^3$ $M^{-1}\,s^{-1}$ (1 M = 1 mol $dm^{-3}$) for $k_1$, $k_2$, and $k_3$, and 0.048, 0.69, and 27 $s^{-1}$ for $k_{-1}$, $k_{-2}$, and $k_{-3}$, respectively, at 25 °C and $I$=0.1. The rate-determining step of the complex formation reactions, which follows the initial formation of ion-pairs, is the dissociation of a water molecule from the inner hydration sphere of the nickel; the glutamate ion acts as a bidentate ligand forming a five-membered chelate ring in the complexes.

Recent developments of relaxation kinetics[1,2] have enabled us to study the rapid reactions involved in the metal-ligand interactions. Complex formation reactions of labile metal ions with various ligands have been widely studied,[3,4] and most of them can be interpreted well by a mechanism involving the rate-determining release of the solvent molecule from the inner coordination sphere of the metal ion.[1,3–5] Particular interest has been directed to the metal complexes with amino acid ligands[6–10] not only from the view point of the coordination chemistry but also of their biological importance as model systems of metal-protein interactions. The metal-amino acid complexes are characterized by the formation of five- or six-membered chelate rings, together with especially large complexation constants compared with those of the other non-chelate-forming agents. The above situation inevitably causes a condition where one must study a reaction system containing two or three kinds of complexes and, therefore, be faced with the relaxation treatment of coupled chemical equilibria.

In the present work, we studied nickel(II)–L-glutamic acid interactions by means of a temperature-jump relaxation technique. Glutamic acid is of interest as a potentially terdentate ligand and because it forms mixed ligand complexes with the other chelating agents. However, in spite of the familiar nature and the biological importance of the acid, few kinetic studies[11] have been done on metal-complexes of this ligand. Any information obtained will be helpful in elucidating the metal-glutamic acid interactions.

## Experimental

All chemicals used were of a reagent grade. Each solution studied was prepared by mixing aqueous stock solutions of $Ni(NO_3)_2$ and a colorimetric pH indicator, adding sodium hydrogen L-glutamate, and finally diluting. Indicators employed were Phenol Red for pH 7.5—8.5 and Phenolphthalein for pH 9.3—9.8. The ionic strength, $I$, of the solutions was kept to 0.1 by the addition of $KNO_3$. The pH of the solution was adjusted with NaOH and/or $HNO_3$.

The temperature-jump apparatus and the experimental procedure have been described previously.[12,13] All the relaxation experiments were carried out at 25±1 °C.

## Results and Treatment of Data

The experimental conditions and the kinetic data observed are summarized in Table 1. All the solutions studied showed a single relaxation phenomenon. The reciprocal relaxation time, $\tau_{obsd}^{-1}$, quoted in Table 1 represents an average of at least four relaxation measurements. The maximum errors are about ±10%. As shown in Table 1, the experiments were carried out in two different pH regions, *i.e.*, around pH 8.0 and 9.8, and the relaxation effect was observed by following the absorbance at the wavelengths 558 (Phenol Red) and 553 nm (Phenolphthalein), respectively. A representative relaxation effect is shown in Fig. 1. Blank solutions of the nickel-indicator and ligand-indicator systems showed no relaxation effect in the same time range. The above fact indicates that the observed relaxation effect is really associated with nickel-ligand interactions.

Under the experimental conditions studied, the formation of nickel(II) glutamate complexes may proceed most generally by the following reaction mechanism:

$$Ni^{2+} + L^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiL \qquad K_1, \qquad (1)$$

$$NiL + L^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NiL_2^{2-} \qquad K_2, \qquad (2)$$

$$NiL_2^{2-} + L^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiL_3^{4-} \qquad K_3, \qquad (3)$$

with the rapid protolytic reactions

$$H_2L \rightleftharpoons H^+ + HL^- \qquad K_{a2}, \qquad (4)$$

$$HL^- \rightleftharpoons H^+ + L^{2-} \qquad K_{a3}, \qquad (5)$$

TABLE 1. KINETIC DATA FOR THE NICKEL-GLUTAMIC ACID SYSTEM AT 25 °C AND $I=0.1$

| $\Sigma$Ni (10$^{-3}$ M) | $\Sigma$L | pH | $\tau^{-1}_{\text{obsd}}$ (s$^{-1}$) | $\tau^{-1}_{\text{calcd}}$ (s$^{-1}$) |
|---|---|---|---|---|
| HIn = Phenol Red[a] | | | | |
| 2.51 | 20.2 | 8.03 | 42.7 | 48.6 |
| 2.51 | 40.6 | 8.03 | 49.1 | 51.0 |
| 5.01 | 5.03 | 8.03 | 37.4 | 38.1 |
| 5.01 | 20.3 | 8.02 | 65.8 | 68.7 |
| 5.01 | 40.3 | 8.04 | 70.0 | 69.5 |
| 10.0 | 10.1 | 8.05 | 66.2 | 57.7 |
| 10.0 | 20.4 | 8.02 | 113 | 112 |
| 10.0 | 30.3 | 7.51 | 102 | 106 |
| 10.0 | 30.3 | 8.02 | 114 | 112 |
| 10.0 | 30.3 | 8.51 | 114 | 109 |
| 10.0 | 40.1 | 8.02 | 108 | 111 |
| 10.0 | 60.4 | 8.03 | 108 | 107 |
| 20.0 | 30.1 | 8.03 | 207 | 194 |
| 20.0 | 41.2 | 8.03 | 207 | 205 |
| 30.1 | 40.4 | 8.02 | 227 | 247 |
| HIn = Phenolphthalein[a] | | | | |
| 5.00 | 10.0 | 9.32 | 58.8 | 64.1 |
| 5.00 | 10.0 | 9.79 | 56.0 | 61.6 |
| 5.00 | 12.5 | 9.80 | 78.8 | 67.1 |
| 5.00 | 15.0 | 9.76 | 80.5 | 70.4 |
| 5.01 | 15.0 | 9.33 | 79.3 | 69.3 |
| 10.0 | 20.0 | 9.79 | 94.8 | 97.8 |
| 10.0 | 25.1 | 9.78 | 105 | 99.3 |
| 10.0 | 30.0 | 9.81 | 103 | 98.7 |
| 10.0 | 35.0 | 9.82 | 113 | 106 |
| 10.0 | 40.0 | 9.80 | 112 | 118 |
| 10.0 | 45.0 | 9.81 | 127 | 136 |
| 10.0 | 50.0 | 9.83[b] | 164 | 166 |
| 20.0 | 40.0 | 9.79 | 176 | 169 |

a) $\Sigma\text{In}=2.5\times10^{-5}$ M. b) $I=0.15$.

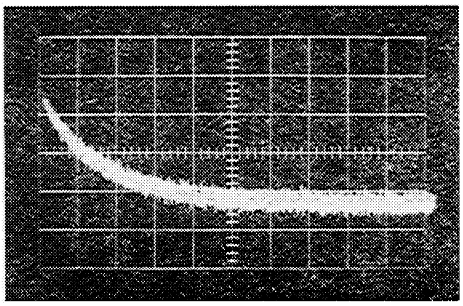

Fig. 1. Relaxation effect in nickel–L-glutamic acid system: $\Sigma\text{Ni}=0.0100$ M, $\Sigma\text{L}=0.0204$ M, pH=8.02, $I=0.1$ with $2.5\times10^{-5}$ M Phenol Red as an indicator. The abscissa scale is 5 ms per division, and the vertical scale is in arbitrary unit of absorbancy. The relaxation effect corresponds to an increase in absorbance with time.

$$\text{Ni}^{2+}+\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{NiOH}^+ \qquad K_{\text{OH}}, \tag{6}$$

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \qquad K_{\text{w}}, \tag{7}$$

$$\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^- \qquad K_{\text{In}}, \tag{8}$$

TABLE 2. EQUILIBRIUM CONSTANTS FOR THE NICKEL-GLUTAMIC ACID SYSTEM AT 25 °C AND $I=0.1$

| | |
|---|---|
| Formation constants of nickel(II) glutamate complexes | $K_1=4.17\times10^5$ [a)]<br>$K_2=1.59\times10^4$ [a)]<br>$K_3=(3.37\pm0.43)\times10^2$ [b)] |
| Dissociation constants of glutamic acid | $\text{p}K_{\text{a2}}=4.18$[a)]<br>$\text{p}K_{\text{a3}}=9.64$[a)] |
| Nickel(II) hydrolysis constant | $\text{p}K_{\text{OH}}=10.07$[c)] |
| Ionic product of water | $\text{p}K_{\text{w}}=13.79$[d)] |
| Indicator constants | $\text{p}K_{\text{In}}=7.74$[e)] (Phenol Red)<br>$\text{p}K_{\text{In}}=9.63$[f)] (Phenolphthalein) |

a) Ref. 14. b) This work. c) Calculated from the value at $I=0$ (Ref. 15) by using the Davies equation for the activity coefficients of the ions (Ref. 16). d) Calculated from the value at $I=0$ (Ref. 17) by using the Davies equation for the activity coefficients of the ions. e) Ref. 18. f) Ref. 19.

where the symbols $\text{L}^{2-}$ and $\text{In}^-$ denote glutamate ion and anionic form of indicator, respectively, and where $K_1$, $K_2$, $K_3$, $K_{\text{a2}}$, $K_{\text{a3}}$, $K_{\text{OH}}$, $K_{\text{w}}$, and $K_{\text{In}}$ are the equilibrium constants for the corresponding reactions. Since the protolytic reactions (4)—(8) reach equilibrium much faster than the metal complex reactions under consideration here, they can be assumed to be in equilibrium at all times.

All the pertinent equilibrium constants used in this study are given in Table 2. In the earlier equilibrium studies of nickel-glutamate systems,[14,20–22] few investigators[21] reported the presence of the tris-complex $\text{NiL}_3{}^{4-}$. Therefore, in the preliminary study, we tried to explain the kinetic data in Table 1 by some mechanisms without Eq. 3; *i.e.*, by the complexation reaction (1) or (2), or by coupling the two, or by adopting the disproportionation reaction $\text{Ni}^{2+}+\text{NiL}_2{}^{2-}\rightleftharpoons 2\,\text{NiL}$. None of them were found to be successful.

By including the three successive complexation equilibria and adopting the usual relaxation treatment, the relaxation times of the system are found to be the solutions of the secular equation:

$$\begin{vmatrix} a_{11}-1/\tau & a_{12} & a_{13} \\ a_{21} & a_{22}-1/\tau & a_{23} \\ a_{31} & a_{32} & a_{33}-1/\tau \end{vmatrix} = 0. \tag{9}$$

By employing the equilibrium relations $K_n=k_n/k_{-n}$ $(n=1, 2, 3)$, the determinant elements $a_{ij}$ are given by

$$\left.\begin{aligned} a_{11} &= k_1\left\{\left(\frac{1-\beta_1}{1+\alpha}\right)[\text{Ni}]+(1-\gamma)[\text{L}]+\frac{1}{K_1}\right\}, \\ a_{12} &= k_1\left\{\left(\frac{1-\beta_2}{1+\alpha}\right)[\text{Ni}]-\frac{1}{K_1}\right\}, \\ a_{13} &= k_1\left(\frac{1-\beta_2}{1+\alpha}\right)[\text{Ni}], \\ a_{21} &= k_2\left\{\left(\frac{1-\beta_2}{1+\alpha}\right)[\text{NiL}]-[\text{L}]\right\}, \\ a_{22} &= k_2\left\{\frac{[\text{NiL}]}{1+\alpha}+[\text{L}]+\frac{1}{K_2}\right\}, \\ a_{23} &= k_2\left\{\frac{[\text{NiL}]}{1+\alpha}-\frac{1}{K_2}\right\}, \end{aligned}\right\} \tag{10}$$

$$\left.\begin{aligned} a_{31} &= k_3\left(\frac{1-\beta_2}{1+\alpha}\right)[\mathrm{NiL_2}], \\ a_{32} &= k_3\left\{\frac{[\mathrm{NiL_2}]}{1+\alpha}-[\mathrm{L}]\right\}, \\ a_{33} &= k_3\left\{\frac{[\mathrm{NiL_2}]}{1+\alpha}+[\mathrm{L}]+\frac{1}{K_3}\right\}, \end{aligned}\right)$$

with

$$\begin{aligned} \alpha &= \{([\mathrm{HL}]+[\mathrm{H_2L}])-([\mathrm{HL}]+2[\mathrm{H_2L}])^2/G\}/[\mathrm{L}], \\ \beta_1 &= \gamma\{2([\mathrm{HL}]+2[\mathrm{H_2L}])-\gamma([\mathrm{L}]+[\mathrm{HL}]+[\mathrm{H_2L}])\}/G, \\ \beta_2 &= \gamma([\mathrm{HL}]+2[\mathrm{H_2L}])/\mathrm{G}, \\ \gamma &= K_{\mathrm{OH}}/(K_{\mathrm{OH}}+[\mathrm{H}]), \\ G &= [\mathrm{HL}] + 4[\mathrm{H_2L}] + [\mathrm{H}] + [\mathrm{OH}] + \gamma[\mathrm{Ni}] \\ &\qquad + [\mathrm{H}][\mathrm{In}]/(K_{\mathrm{In}}+[\mathrm{H}]), \end{aligned}$$

where the square brackets indicate the molar concentration at equilibrium, and where the charges of the ions are omitted for the sake of simplicity.

Solving Eq. 9, we obtain three relaxation times $\tau_1$, $\tau_2$, and $\tau_3$ ($\tau_1<\tau_2<\tau_3$) as functions of the determinant elements (see Appendix). Since we measured only one relaxation time in each solution studied, we must assign it to one of the three relaxation times predicted by the mechanism. Therefore, we tested the above reaction mechanism for the three cases, in each of which all the experimental data in Table 1 are exclusively associated with only one relaxation time, *i.e.*, (i) $\tau_1$, (ii) $\tau_2$, or (iii) $\tau_3$. The simulation analyses were carried out on computer by iterating the four adjustable parameters $K_3$, $k_1$, $k_2$, and $k_3$ and by comparing the computed $\tau^{-1}$ with the values experimentally observed. The adjustable parameters were optimized by minimizing the root-mean-square percentage deviation between the computed and the observed values of $\tau^{-1}$.

The above simulation analyses revealed that only case (i) gives results consistent with the experiment; case (ii) and (iii) cannot be fitted to the experimental results. As shown in Table 1, the calculated $\tau_1^{-1}$ values (denoted by $\tau_{\mathrm{calcd}}^{-1}$) agree fairly well with the observed values (r.m.s. % deviation=7.2). The $K_3$ value determined is shown in Table 2. Considering the differences in ionic strengths, the value garees well with that reported by Gergely and Farkas in their equilibrium studies:[21] $K_3=437$ at 25 °C and $I=0.2$. The rate constants determined are shown in Table 3. The contribution of each successive complexation reaction to the relaxation process can be realized from the uncertainty interval of the pertinent rate constant $k_n$ in Table 3.

In the above data treatment, reaction pathways *via* protonated ligands $\mathrm{HL^-}$ and $\mathrm{H_2L}$ are omitted. Reactants of these types lead to additional terms in $k_n$ and $k_{-n}$. These terms are proportional to either hydrogen-ion concentration or the square of it. Nevertheless, the same set of rate constants gave uniformly good agreement between $\tau_{\mathrm{obsd}}$ and $\tau_{\mathrm{calcd}}$ in the pH range 7.5—9.8, without including additional hydrogen-ion dependent terms. We may therefore conclude that, within the experimental error, the major contribution to the relaxation time involves only terms arising from reactions (1)—(3). An additional experiment for the solution containing 0.01 M nickel and 0.01 M glutamic acid, using Methyl Red indicator, at pH 5, where the concentration of glutamate ion $\mathrm{L^{2-}}$ is of the order of $10^{-7}$ M, did not show any relaxation effect.

Table 3. Kinetic results for the formation of nickel(II) glutamate complexes at 25 °C and $I=0.1$

| $n$ | $k_n/\mathrm{M^{-1}\,s^{-1}}$ | $k_{-n}/\mathrm{s^{-1}}$ |
|---|---|---|
| 1 | $(2.0\pm0.3)\times10^4$ | $(4.8\pm0.7)\times10^{-2}$ |
| 2 | $(1.1\pm0.2)\times10^4$ | $(6.9\pm1.4)\times10^{-1}$ |
| 3 | $(9.2\pm0.5)\times10^3$ | $(2.7\pm0.4)\times10$ |

## Discussion

As shown in Table 3, the rate constants $k_n$ are all of the same order of magnitude and show a slightly decreasing tendency of $k_1>k_2>k_3$, which may reflect the electrostatic interactions between the reaction partners. The above result indicates that the successive complex formation reactions (1)—(3) proceed *via* a similar process. The three glutamate ions in the tris-complex $\mathrm{NiL_3^{4-}}$ are very likely to be all bidentate, forming five-membered chelate rings, with the $\gamma$-carboxylato groups remaining uninvolved in complexation. Therefore, the kinetic result suggests that the glutamate ions in the mono- and bis-complexes NiL and $\mathrm{NiL_2^{2-}}$ act as bidentate ligands similar to those in the tris-complex. On the contrary, if the mono- and/or bis-complex contained terdentate ligand, the formation of $\mathrm{NiL_2^{2-}}$ or $\mathrm{NiL_3^{4-}}$ must involve the cleavage of at least one nickel-ligand bond, and therefore the rate constant $k_2$ or $k_3$ would be very different from $k_1$. This is inconsistent with the present result. The above structural assignment for nickel glutamate complexes is also supported by some equilibrium studies.[21,22]

The $k_n$ values in Table 3 are close to the corresponding rate constants for nickel complexes with univalent $\alpha$-amino acid ligands such as glycinate,[6] $\alpha$-alanate,[8] and $\alpha$-aminobutyrate:[9] $(1.0—2.0)\times10^4$, $(1.5—6.0)\times10^4$, and $(3.0—4.2)\times10^4\ \mathrm{M^{-1}\,s^{-1}}$ for $k_1$, $k_2$, and $k_3$, respectively, at 20—25 °C and $I=0.1$—0.15. On the other hand, the $k_1$ value in Table 3 is significantly smaller than those with bivalent anionic ligands such as oxalate,[23] malonate,[24] and cysteine:[25] $(7.0—15)\times10^4\ \mathrm{M^{-1}\,s^{-1}}$ at 20—25 °C and $I=0.1$. According to the widely accepted mechanism of metal-complex formation,[3-5] the rate constants $k_n$ are described in terms of the first-order rate constant $k_\mathrm{o}$ for the dissociation of water from the inner hydration sphere of the metal and the association constant $K_\mathrm{o}$ of the ion-pair as: $k_n=K_\mathrm{o}k_\mathrm{o}$. The similarity of the $k_n$ values in Table 3 to those for the univalent anionic ligands indicates that glutamate ion behaves virtually as an univalent anionic ligand for the ion-pair formation. This aspect seems to be reasonable since the negative charge of $\gamma$-carboxylato of the ligand resides on a site remote from the chelate-forming groups and the metal ion sees an effective charge less than −2 owing to the electrostatic shielding of the large ligand.[7] Through the formal estimation of $K_0$ (for 2-1, 1-1, and 0-1 valent ion-pairs) by using Fuoss equation[26] and by setting the minimum approach distance between the reaction partners at 5 Å, the rate constants $k_0$ of ligand substitution were calculated to be $1.0\times10^4$, $1.4\times10^4$, and $2.9\times10^4\ \mathrm{s}^{-1}$ from $k_1$, $k_2$, and $k_3$, respectively, in Table 3. All these values are consistent with the first-order rate constant of the water exchange of nickel ion as determined by an NMR technique:[27] $3\times10^4\ \mathrm{s}^{-1}$ at 25 °C. The tendency of the increasing water release rate with the higher complexes agrees well with those found in the other nickel-amino acid complexes,[6–9] indicating a significant effect of glutamate ions on the enhancement of the rate of water replacement.

The conclusion is that glutamate ion acts as a bidentate ligand in the nickel complexes and that the formation of the complexes is rate-determined by the release of a coordinated water molecule from the metal rather than by the formation of a chelate-ring closure.

## Appendix

Expanding Eq. 9, we obtain the cubic equation

$$\tau^{-3} \quad a\tau^{-2} + b\tau^{-1} - c = 0, \tag{A1}$$

where

$$\begin{aligned} a &= a_{11} + a_{22} + a_{33}, \\ b &= (a_{11}a_{22} - a_{12}a_{21}) + (a_{22}a_{33} - a_{23}a_{32}) \\ &\quad + (a_{33}a_{11} - a_{31}a_{13}), \\ c &= a_{11}(a_{22}a_{33} - a_{23}a_{32}) + a_{12}(a_{23}a_{31} - a_{21}a_{33}) \\ &\quad + a_{13}(a_{32}a_{21} - a_{31}a_{22}). \end{aligned}$$

The secular equation 9 has only real positive eigenvalues of $\tau^{-1}$.[1,5] Thus, by solving Eq. Al, the three relaxation times are given by[28]

$$\begin{aligned} 1/\tau_1 &= a/3 + 2\sqrt{p}\cdot\cos(\theta/3), \\ 1/\tau_2 &= a/3 - 2\sqrt{p}\cdot\cos\{(\theta+\pi)/3\}, \\ 1/\tau_3 &= a/3 - 2\sqrt{p}\cdot\cos\{(\theta-\pi)/3\}, \end{aligned} \tag{A2}$$

with

$$\begin{aligned} \theta &= \cos^{-1}(q/2p^{3/2}) && (0 \leqq \theta \leqq \pi), \\ p &= (a^2 - 3b)/9 && (p > 0), \\ q &= (2/27)a^3 - ab/3 + c. \end{aligned}$$

As can be realized easily from Eq. A2, we have the inequality relations $\tau_1^{-1} > \tau_2^{-1} > \tau_3^{-1}$ and $\tau_1^{-1} > a/3 > \tau_3^{-1}$.

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