BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2961—2962 (1975)

An Equilibrium Study of the Formation of Mixed-Ligand Nickel(II)–Aminopolycarboxylate Complexes

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(Received March 22, 1975)

Synopsis. The equilibria for the formation of 1 : 1 : 1 ratio mixed-ligand complexes of nickel(II)-NTA, HIDA, and -ethylenediamine-*N,N'*-diacetate (EDDA) complexes with the glycinate (Gly), glutamate (Glut), and aspartate (Asp) anions were studied by determining the effects of the Gly, Glut, and Asp anions on the rates of the substitution reactions of nickel(II)-NTA, -HIDA, and -EDDA complexes with EDTA-OH or DTPA.

Recently the importance of the formation of mixed-ligand complexes has been recognized, and a large number of studies have been carried out for a better understanding of the mixed-ligand complex formation.[1–3] The present author has also studied the equilibria for the formation of mixed-ligand complexes between ammonia and metal (II)-aminopolycarboxylate complexes.[4,5] In this paper, the mixed-ligand complex formation equilibria between the nickel(II)–aminopolycarboxylate complexes and the Gly, Glut, and Asp anions will be studied by investigating their effects on the rates of the substitution reactions of nickel(II)–aminopolycarboxylate complexes.

Experimental

Reagents. The EDDA, NTA, Glut, Gly, Asp, EDTA-OH, and DTPA used in this study were recrystallized as their acids from their aqueous solutions. The preparation and recrystallization of the acid form of HIDA were described previously.[6] The other chemicals used were of analytical reagent-grades and were used without further purification.

Apparatus and Experimental Procedures. The polarographs and the dropping mercury electrode (DME) used for the measurement of the DC current-voltage curves and the current-time curves were the same as those described previously.[6,7] The pH of the solution was measured with a glass electrode in combination with a pH meter (Hitachi-Horiba Model F-7). All the experimental procedures used in the kinetic study have been described previously.[8] In this study, all the measurements were conducted in solutions with an ionic strength of 0.30 ($NaClO_4$) at 25 °C. No buffer reagent was used, because the sample solutions always contained a large excess of uncomplexed aminopolycarboxyfate and had a sufficient buffer capacity in the pH range studied ($9.00<\mathrm{pH}<10.00$). The reaction rates were determined by observing the change in the dissolution wave due to the uncomplexed DTPA or EDTA-OH under the experimental conditions where all the reactions could be treated as pseudo first-order reactions. The forward apparent rate constant, k_{ap}, was determined from the slope ol the linear relation between log (i_0/i_t) and time, t.[9]

Results and Discussion

Previously,[7] the present author reported that the rate of the reaction of EDTA with the nickel(II)–EDDA complex is reduced appreciably by the addition of Gly; he ascribed this to the formation of a mixed-ligand complex involving the Gly anion. As in the case of the EDTA reaction with the nickel(II)–EDDA complex in the presence of the Glut or Asp anion also gave a k_{ap} value which was independent of the concentrations of the uncomplexed DTPA and EDDA, but proportional to the total concentration of the nickel(II) ion$[\mathrm{Ni(II)}]_t$. Furthermore, the Glut and Asp anions reduced the reaction rate and the plot of k_{ap}^{-1} against the uncomplexed Glut or Asp concentration, $[A^{m-}]$, invariably gave a straight line, with an intercept of a finite value (Fig. 1). In view of the conclusion obtained in the EDTA reaction with the nickel(II)–EDDA complex in the presence of the Gly anion, these findings suggest that the Glut and Asp anions also form a 1 : 1 : 1 ratio mixed-ligand complex with the nickel(II)–EDDA complex and that the rapid dissociation of the Glut or Asp anion from the mixed complex precedes the slow reaction of the DTPA anion with the 1 : 1 ratio nickel(II)–EDDA complex. Thus, the k_{ap} at a given pH should be given by the following relation:

$$k_{ap} = k\cdot[\mathrm{Ni(II)}]_t/(1+K^{A}_{MXA}\cdot[A^{m-}]) \qquad (1)$$

where K^{A}_{MXA} means the equilibrium constant for the formation of a mixed-ligand complex from the nickel(II)–EDDA complex and the Glut or Asp anion. Therefore, the K^{A}_{MXA} value can be determined from

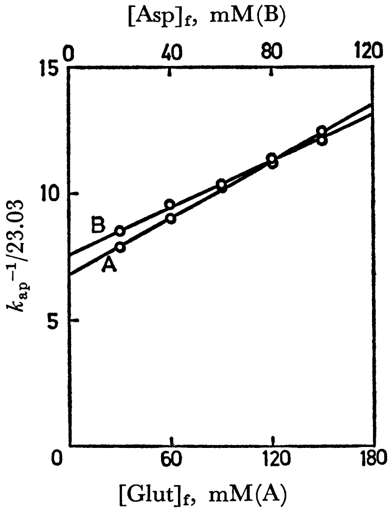

Fig. 1. The plot of the reciprocal of k_{ap} for the reaction of nickel(II)-EDMA complex with DTPA against the concentrationof uncomplexed Gly or Asp. $\mu=0.30$, 25 °C, pH=9.35, $[\mathrm{DTPA}]_i=1.0$ mM $[\mathrm{EDDA}]_f=10.0$ mM, $[\mathrm{Ni(II)}]_t=10.0$ mM
A) $[\mathrm{Gly}]_f$ ranged from 30 to 150 mM.
B) $[\mathrm{Asp}]_f$ ranged from 20 to 100 mM.

the ratio of the slope to the intercept of the linear relation between k_{ap}^{-1} and $[\mathrm{A}^{m-}]$. Although no experimental result is shown here, k in Eq. (1) could be determined to be $(k_\alpha+k_\beta\cdot[\mathrm{H}^+])/(\alpha_\mathrm{H})_\mathrm{Y}$[9] from a systematic investigation of the pH effect on the reaction rate. The $K^{\mathrm{A}}_{\mathrm{MXA}}$ values obtained from the slope and intercept of the linear relation in Fig. 1 are listed in Table 1, together with that for the EDDA∼Gly system.[7] The reactions of DTPA with the nickel(II)–NTA complex and of EDTA-OH with the HIDA complex in solutions containing the Gly, Glut, or Asp anion also showed kinetic profiles quite similar to that of the DTPA reaction with the nickel(II)-EDDA complex in the presence of Glut or Asp. In these reactions, the reaction rates of the Gly, Glut, and Asp anions were also appreciably reduced, and the plot of k_{ap}^{-1} *versus* the concentration of the Gly, Glut or Asp anion, $[\mathrm{A}^{m-}]$ at a given pH invariably gave a straight line with an intercept of a finite value. A typical result obtained for the Asp system is reproduced in Fig. 2. In the light of the coordination natures of the nickel(II) ion and the NTA and HIDA anions, the above fact also suggests the formation of a 1 : 1 : 1 ratio mixed-ligand complex involving the Gly, Glut, or Asp anion, which is in a rapid equilibrium with the 1 : 1-ratio NTA or HIDA complex involved in the rate-determining steps. With the NTA and HIDA anions, the nickel(II) ion forms a 1 : 2 ratio complex. Therefore, the k_{ap} value for the NTA and HIDA systems should be given by $[\mathrm{Ni(II)}]_\mathrm{t}\cdot k/(1+K_2'\cdot[\mathrm{X}]_\mathrm{f}+K^{\mathrm{A}}_{\mathrm{MXA}}\cdot[\mathrm{A}^{m-}])$ in place of Eq. (I). Here, K_2' denotes the conditional second successive formation constant of the nickel(II)–NTA or –HIDA complex, and $[\mathrm{X}]_\mathrm{f}$, the concentration of uncomplexed NTA or HIDA. Then, the $K^{\mathrm{A}}_{\mathrm{MXA}}$ values for the NTA and HIDA systems were determined from the ratio of the slope to the intercept of the linear relation between k_{ap}^{-1} and $[\mathrm{A}^{m-}]$, with the aid of the $K^{\mathrm{A}}_{\mathrm{MXA}}=(1+K_2'\cdot[\mathrm{X}]_\mathrm{f})\times$slope/intercept relation. In the case of the HIDA system, no confirmative evidence which suggests the formation of a mixed-ligand complex involving the Gly anion could be obtained under the present experimental conditions. The $K^{\mathrm{A}}_{\mathrm{MXA}}$ values obtained for the NTA and HIDA systems are also listed in Table 1. In all the systems studied in this paper, the $K^{\mathrm{A}}_{\mathrm{MXA}}$ values determined at various solution pH's showed a satisfactory agreement with each other.

Table 1. The $K^{\mathrm{A}}_{\mathrm{MXA}}$ values ($\mu=0.30$, 25 °C)

System	log $K^{\mathrm{A}}_{\mathrm{MXA}}$	System	log $K^{\mathrm{A}}_{\mathrm{MXA}}$
EDDA-$\mathrm{NH_3}$	1.62[11]	NTA-Gly	3.68
EDDA-Gly	1.12[8]	NTA-Glut	3.57
EDDA-Glut	1.32	NTA-Asp	3.92
EDDA-Asp	1.30	HIDA-Glut	4.84
		HIDA-Asp	4.86

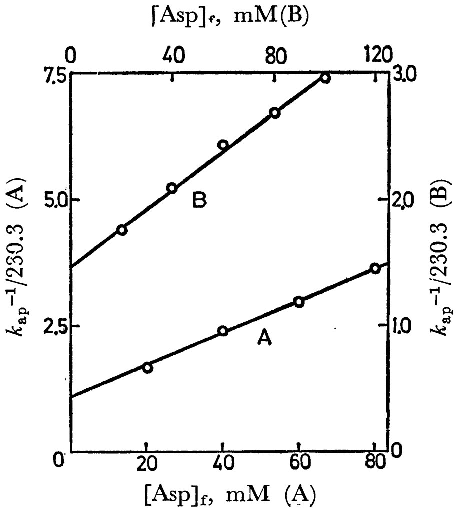

Fig. 2. The effect of aspartate on the rates of the reactions of the nickel(II)-NTA complex with DTPA and of the nickel-HIDA complex with EDTA-OH. $\mu=0.30$, 25 °C, $[\mathrm{Asp}]_\mathrm{f}$ ranged from 20 to 100 mM

A) NTA system pH=9.73, $[\mathrm{NTA}]_\mathrm{f}=20.0$ mM $[\mathrm{Ni(II)}]_\mathrm{t}=10.0$ mM, $[\mathrm{DTPA}]_\mathrm{i}=1.0$ mM.

B) HIDA system pH=9.58, $[\mathrm{HIDA}]_\mathrm{f}=28.0$ mM $[\mathrm{Ni(II)}]_\mathrm{t}=6.0$ mM, $[\mathrm{EDTA\text{-}OH}]_\mathrm{i}=0.6$ mM.

Ho *et al.*[10] reported in their NMR study of mixed 1 : 1 : 1 EDDA complexes of the nickel(II) ion with the Glut and Asp anions that the mixed-ligand complex has the trans-form, and that the Glut and Asp anions in the complex are bonded to the nickel(II) ion through the glycinate chelate ring. The finding that the $K^{\mathrm{A}}_{\mathrm{MXA}}$ value for the Gly∼EDDA system is nearly identical with those for the Glut∼ and Asp∼EDDA systems may support their conclusion. As is shown by the data in Table 1, the $K^{\mathrm{A}}_{\mathrm{MXA}}$ values for the Gly, Glut, and Asp systems are slightly smaller than that for the 1 : 1 : 1 mixed complex of ammonia.[11] This is probably ascribable to the unfavourable entropy change due to the formation of the charged mixed complex from the neutral parent complex. The mixed 1 : 1 : 1-ratio NTA and HIDA complexes with the Gly, Glut, and Asp anions also have almost the same $K^{\mathrm{A}}_{\mathrm{MXA}}$ values. This may also indicate that all three aminoacid anions in the mixed-ligand complex coordinate to the nickel(II) ion through a Gly chelate ring.

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