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## REDUCTION MECHANISMS FOR Ni(II) COMPLEXES WITH DIAMINO ACIDS AND HISTIDINE AT A DROPPING MERCURY ELECTRODE

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Reduction of Ni(II) ions in the presence of potentially terdentate diamino acids (2,3-diaminopropionic acid, 2,4-diaminobutyric acid, histidine) was studied polarographically. The complex species reduced on a mercury electrode and their electrochemical parameters were determined. Electrochemical behaviour of the particular species strongly depends on the donor set bound to the metal ion. Evaluated stability constants show that the studied systems have different thermodynamic stabilities even for the same donor system involved when chelate rings differ in size.

*Keywords:* Ni(II); S-diamino acids; polarography; reduction mechanism

### INTRODUCTION

The electrochemical behaviour of Ni(II) species is strictly dependent on the nature and concentration of the species reduced on an electrode as well as on the concentration of free ligand. In the case of dicarboxylic acid complexes with oxalates or malonates,<sup>1,2</sup> the first species to undergo reduction on a mercury electrode is reduced in an irreversible process at more negative potentials than that of the aquaion. Ni(II) complexes with nitrogen c-ligands like NH<sub>3</sub>, pyridine or aminosugars<sup>3–9</sup> are reduced at more positive potentials than the aquaion and the reduction is more reversible. It should be mentioned here that in many cases the mechanisms are far from understood.

In the case of amino acids, chelation occurs *via* the amino group and the carboxylate function. Nitrogen coordination shifts reduction potential to the more positive values when compared to the aquaion, while the carboxylate function has the opposite effect thus diminishing the 'positive shift'.<sup>10,11</sup>

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The presence of a third coordinating group in the ligand molecule could also have a distinct effect on the reduction potential of the species reduced on a mercury electrode. Ni(II) binding to aspartic acid *via* the  $\{\text{NH}_2, \alpha\text{-COO}^-, \beta\text{-COO}^-\}$  donor set causes the complex formed to be reduced at distinctly more negative potentials than the aquaion.<sup>11</sup> Since the effect of the coordinated amino function as the third bound donor has not yet been reported results obtained for two diamino acids, 2,3-diaminopropionic and 2,4-diaminobutyric acid, as well as histidine having imidazole nitrogen additional to the  $\{\text{NH}_2, \text{COO}^-\}$  binding site, are presented below.

Spectroscopic and potentiometric studies have shown<sup>12-18</sup> that coordination equilibria in all these systems are relatively complicated due to a variety of possible binding modes in the complexes formed including monodentate ( $\text{COO}^-$ ), bidentate (glycine-like or diamino coordination) and terdentate coordination. Detailed analysis of the reduction potentials and limiting currents permitted an evaluation of the stoichiometry of the complexes formed as well as reduction parameters for the particular species. The effect of the second coordinating amino group in terdentate complexes on the reduction mechanism is also discussed.

## EXPERIMENTAL

Electrode processes were studied with DC (direct current) and DP (differential pulse) polarography on Radelkis OH-105 and Telpod PP-04 polarographs. A dropping mercury electrode (DME) was used as a working electrode and a saturated calomel electrode as a reference electrode. The mercury container was placed at a height of 45 cm, the mercury flow-rate was  $1.965 \text{ mg s}^{-1}$  and the drop time 4.5 s. The saturated calomel electrode was connected to the polarographic cell with a salt bridge filled with saturated  $\text{NaClO}_4$ . All measurements were performed at  $25^\circ\text{C}$  and at ionic strength  $0.1 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ). The concentration of Ni(II) was fixed at  $1$  or  $2 \times 10^{-4} \text{ mol dm}^{-3}$  and the concentration of ligands varied from  $10^{-4}$  to  $10^{-2} \text{ mol dm}^{-3}$ . All stock solutions were prepared with analytical reagent grade chemicals. Ligands had the *S* configuration Argon was bubbled through solutions to remove oxygen. Polyvinyl alcohol was used to suppress polarographic maxima; pH was adjusted with NaOH or  $\text{HClO}_4$ .

## RESULTS AND DISCUSSION

### Ni(II)-2,3-diaminopropionic acid (Dapa)

Three DC reduction waves are observed in the Ni(II)-Dapa system. At pH below 3.3 the major complex reduced at the electrode at  $-0.981 \text{ V}$  is the aquaion.

Above pH 3.3 the new wave appears at a more positive potential,  $-0.85$  V, whose limiting current increases to pH 5. Between pH 5 and 7.5 this single reduction wave shifts towards more negative potentials and above pH 7.5 its limiting current decreases to about 60% of that observed for the aquaion.

In DPP measurements of Ni(II)-Dapa three peaks are observed, including that at  $-1.010$  V corresponding to reduction of the aquaion. The two other peaks, at  $-0.872$  V, observed below pH 5 and at  $-0.952$  V, observed above pH 5, correspond to the reduction of two complex species. The latter peak decreases in height above pH 7.

Logarithmic analysis of the reduction wave of the first complex formed, which is placed at most positive potential, (pH 5), gives a slope ( $RT/\alpha nF$ ) of 41 mV. When pH increases this reduction wave changes indicating that its shape consists of two closely placed waves.<sup>19,20</sup> Above pH 6.5 it becomes single wave with slope of 52 mV corresponding to the reduction of one Ni(II) species with Dapa.

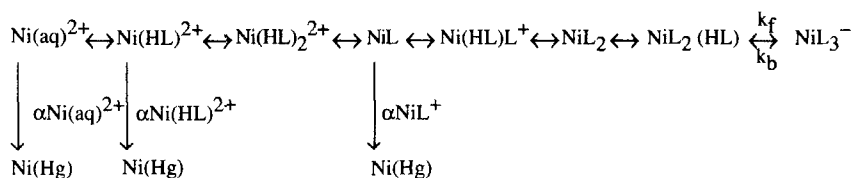
The first reduction wave with slope of 41 mV corresponds most likely to the reduction of the bidentate  $\text{Ni}(\text{HL})^{2+}$  complex with glycine-like,  $\{\text{NH}_2, \text{COO}^-\}$ , coordination. This type of slope is usually observed for reduction waves of Ni(II) complexes with simple bidentate 1:1 amino acid complexes.<sup>11</sup> The second wave with slope of 52 mV is similar to that of the reduction of  $\text{NiL}_2$  species with simple amino acids. In the case of the Ni(II)-Dapa system it may correspond to the reduction of two complexes,  $\text{NiL}^+$  with  $\{\alpha\text{-NH}_2, \beta\text{-NH}_2 \text{COO}^-\}$  coordination and/or  $\text{Ni}(\text{LH})_2^{2+}$  species with two ligand molecules bound through  $\{\text{NH}_2, \text{COO}^-\}$ . The reduction potentials of both complex species should be similar to each other. Although removing two bidentate ligands from  $\text{Ni}(\text{LH})_2^{2+}$  may cost more energy than one tridentate Dapa from  $\text{NiL}^+$ , the presence of two positively charged  $\beta(\text{NH})_3^+$  groups in  $\text{Ni}(\text{LH})_2^{2+}$  would compensate for this difference by neutralising the negative potential of a mercury electrode. However, the contribution of the  $\text{Ni}(\text{LH})_2^{2+}$  species should be of minor importance because of its low concentration in the solutions studied.

At high pH in solutions with a high excess of ligand the evaluated difference of the average numbers of ligands bound to complex undergoing reduction ( $\text{NiL}^+$ ) and that being the major species in solution<sup>21</sup> equals 1.67, suggesting that the dominant complex in strongly basic solutions is the  $\text{NiL}_3^-$  species. The presence of this complex leads to a kinetically controlled electrode process (reduction waves decreases at pH above 7.5). The rate constant for  $\text{NiL}_3^-$  dissociation ( $k_b$ ) calculated from the equation for the kinetically controlled limiting current<sup>22</sup> is  $k_b = 10^{5.28} \text{ s}^{-1}$ .

Stability constants for  $\text{Ni}(\text{LH})_2^{2+}$  and  $\text{NiL}^+$  were calculated from the mol fraction of Ni(II) aquaion evaluated from the DPP peak heights at various pH

values and the constant ligand concentration ( Table I). The stability constants of other complexes were calculated using the equation for the reduction wave of irreversible processes.<sup>23</sup>

The results obtained above suggest the following reduction mechanism in the Ni(II)-Dapa solutions.



### Ni(II)-2,4diaminobutyric acid (Daba)

In Ni(II)-Daba solutions two DC reduction waves are observed. At pH 4.3–5.8 the reduction wave of the aquaion accompanies the reduction wave of complex species at more positive potentials. The latter is a minor one when compared to metal ion reduction (up to 30% of height). Above pH 6.8 there is only one reduction wave of complex species; this moves towards more negative potentials with increasing pH.

Four peaks are observed in DPP measurements of Ni(II)-Daba solutions including that corresponding to the aquaion reduction and three others which are assigned to reductions of complex species. The free ion is reduced at  $-1.012$  V and complexes at  $-0.867$  (pH below 5.8),  $-0.998$  (pH 5.7–6.7) and  $-1.07$  V (pH above 6.3). The potential of the latter peak moves towards more negative values with increasing pH. Assignment of the reduction peaks is similar to that discussed above for the Ni(II)-Dapa system, *i.e.*, the peak at  $-0.867$  V corresponds to the reduction of  $\text{Ni(HL)}^{2+}$  and the two others to  $\text{Ni(HL)}_2^{2+}$  and  $\text{NiL}^+$ , respectively.

The difference in the average ligand number between the complex reduced at the DME and the dominant species present at high pH evaluated from the plot of  $\Delta E_{1/2}$  vs  $f(\log([L^-]_{\text{free}}))$ <sup>21</sup> is only 1.05, indicating that the dominant complex at high pH in solutions with high ligand excess is the  $\text{NiL}_2$  species. This result is a major difference to the Ni(II)-Dapa system for which in these conditions  $\text{NiL}_3^-$  was observed (*vide supra*). Stability constants evaluated in a similar way as those above for Dapa complexes are collected in Table I. The results obtained suggest the following reduction mechanism.

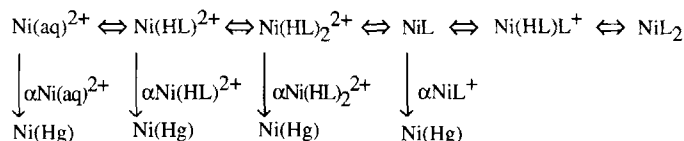


TABLE I Proton dissociation constants for the ligands and stability constants for their complexes with Ni(II).

Ligand	pK		log $\beta$										Ref	
	$\alpha$ -COOH	sidechain	$NH_3^+$	$MH_2L^{3+}$	$M(HL)^{2+}$	$ML^+$	$M(HL)_2^{2+}$	$ML(HL)^+$	$ML_2$	$M(HL)_3^{2+}$	$ML(HL)_2^+$	$ML_2(HL)$		$ML_3^-$
apa	1.32	9.39	6.69		3.93	8.48				15.27				12
					4.035	8.159	7.514	11.669	15.156					14
					4.04	8.13	7.58	11.65	15.17			17.07	18.35	15
					4.11	8.36	7.50	11.59	15.12			16.50	18.06	this work
aba	1.89	10.23	8.23		4.538	8.909		12.637	15.965					14
					4.66	8.97	8.69	12.89	16.34	12.86	16.15	19.26	19.80	15
					4.58	8.91	8.60	12.75	15.60					this work
s	1.7	6.02	9.09			8.69			15.58					17
						8.66			15.50					16
					3.16	8.636		11.37	15.456					18
				1.73	3.30	8.80		11.00	15.35					this work

TABLE II Electrochemical parameters for different species reduced at the dropping mercury electrode in the Ni(II)-ligand systems<sup>a</sup>.

Ligand	$-E_p(V)$ (vs SCE)					$2.3RT/0.059F(mV)$					
	$M^{2+}$	$MH_2L^{3+}$	$MHL^{2+}$	$ML^+$	$M(HL)_2^{2+}$	$ML_2$	$M^{2+}$	$MH_2L^{3+}$	$MHL^{2+}$	$ML^+$	$(M(HL)_2)^{2+}$
Dapa	1.010		0.872	0.952			71	41	52		
Daba	1.012		0.867	1.07-1.26	0.998		72	42	52	52	
His	1.013	1.052		0.84-0.93		1.03-1.31	72	86-90	53		53

<sup>a</sup> Dapa:  $K^0_{Ni(aq)^{2+}} = -0.981 V$ ; Dapa:  $K^0_{Ni(aq)^{2+}} = 1.44 \times 10^{-3} \text{ cm s}^{-1}$ ,  $k^0_{NiL^+} = 5.03 \times 10^{-2} \text{ cm s}^{-1}$ ; Daba:  $k^0_{Ni(aq)^{2+}} = 1.44 \times 10^{-3} \text{ cm s}^{-1}$ ,  $k^0_{Ni(HL_2)^{2+}} = 1.58 \times 10^{-3} \text{ cm s}^{-1}$ ,  $k^0_{NiL^+} = 2.87 \times 10^{-3} \text{ cm s}^{-1}$ .

### Ni(II)-L-histidine (His)

Below pH 3.5 a new DC reduction wave is observed at more negative potentials and of much lower limiting current than that of the aquaion and its slope is 86–90 mV. Above pH 3.5 a second reduction wave appears at  $-0.84$  V and its height increases, reaching a maximum at pH 4.68. Further increase of pH causes a shift of the reduction potential towards more negative values and a decrease of the limiting current until it vanishes at pH  $\sim 7$ ; a new wave appear at  $-1.03$  V with a slope of 53 mV. The peaks seen in DPP behave very similarly to the DC reduction waves and their parameters are given in Table II.

The reduction wave observed below pH 3.5 consist of two waves including that of aquaion reduction. The second species reduced at DME is probably the minor  $\text{NiH}_2\text{L}^{3+}$  complex with monodenate coordination through the carboxylate function. At higher pH imidazole and amino nitrogen coordinate and  $\text{NiL}^+$  is formed. This complex is reduced at more positive potential values (Table I). The second reduction wave corresponds to the reduction of  $\text{NiL}_2$ , while  $\text{NiHL}^{2+}$  and  $\text{NiL(HL)}^+$  complexes play a minor role as their concentrations in solution are very low. DC reduction waves are diffusion controlled allowing evaluation of the stability constants collected in Table I.

### Coordination Equilibria in Ni(II)-Terdentate Amino Acid Solutions

The studies on Ni(II) complexes with terdentate ligands have shown that electrochemical behaviour of the particular species strongly depends on the donor system bound to the metal ion. The only polarographically well studied terdentate Ni(II) complex system with amino acids is that involving Asp with coordination through the  $\{\text{NH}_2, \alpha\text{-COO}^-, \beta\text{-COO}^-\}$  donor set.<sup>11</sup> In the systems studied here, terdentate coordination is realised *via*  $\{2 \times \text{N}, \text{COO}^-\}$ . The two chelating rings are 5 + 5 for Dapa and 5 + 6 for Daba and His, respectively. Thus, in the studied systems one can also expect different thermodynamic stabilities of the complexes formed for similar or the same donor set bound to metal ion<sup>14</sup> (Table I).

At low pH- both Dapa and Daba form protonated species  $\text{Ni(HL)}^{2+}$  and  $\text{Ni(HL)}_2^{2+}$  with bidentate  $\{\alpha\text{-NH}_2, \text{COO}^-\}$  coordination. Increasing pH leads to deprotonation and coordination of the second amino group and formation of  $\text{NiL}^+$ ,  $\text{NiL(HL)}^+$  and  $\text{NiL}_2$ . It is interesting to note the higher stability of the  $\text{NiL}^+$  complex for Daba when compared to Dapa (Table I). This higher effectiveness of Daba terdentate binding acts against the formation of  $\text{NiL}_3^-$  for this ligand.

Histidine is a typical terdentate ligand which is extremely important for Ni(II) biochemical behaviour. In spite of a huge amount of data there are still



some controversy concerning the competition between the amino and imidazole nitrogens in the anchoring of the metal ion,<sup>24</sup> which may be important in establishing the binding sites in protonated NiHL<sup>+</sup>-species<sup>14,25</sup> Polarographic data obtained in this work at low pH, 2–3.5, suggest the formation of a monodentate (likely carboxylate bound) species. Its concentration is very low and its formation was suggested earlier from NMR data.<sup>31</sup>

### Reduction of Ni(II)-Amino Acid Complexes

In all studied cases the first complex with nitrogen coordination (usually the {NH<sub>2</sub>, COO<sup>-</sup>} chelate) is reduced at more positive potentials than the aquaion (Table II). In the case of Dapa and Daba this concerns the NiHL<sup>2+</sup> species with glycine-like binding. The same phenomenon is observed for complexes with bidentate amino acids Gly, Glu or Asn. However, the reduction potential of the Dapa or Daba NiHL<sup>2+</sup> complex, which occurs at the same potential, is shifted towards positive potentials much more distinctly than those observed for simple amino acids. This clearly indicates the role of protonated  $\beta$  or  $\gamma$ -amino groups in facilitating complex reduction at DME. Comparison of the potentials for NiL<sup>+</sup> reduction for Dapa and Daba (Table II) shows that the Daba species is reduced at more negative values (55 mV). This is a result of the more stable terdentate coordination of Daba with 5 + 6 chelate rings.

In Ni(II)-His solutions the concentrations of protonated complexes are low (around 10%) and their reduction waves are difficult to observe. The most positive reduction potentials observed is for terdentate NiL<sup>+</sup> species with {NH<sub>2</sub>, N<sub>imid</sub>, COO<sup>-</sup>} binding. This complex undergoes reduction at more positive potentials than those observed for the corresponding NiL<sup>+</sup> species of Daba and Dapa. This is, most likely, the result of the  $\pi$ -acceptor properties of the imidazole ring in the His complex.

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