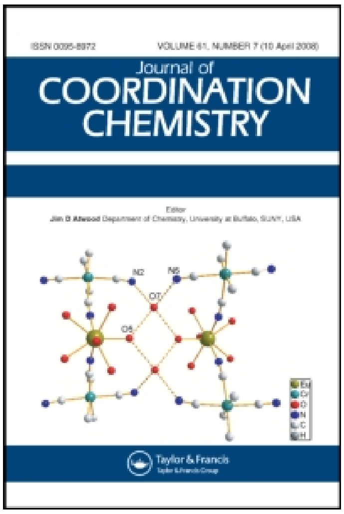

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REDUCTION OF Co(II) COMPLEXES WITH SELECTED AMINO ACIDS ON A DROPPING MERCURY ELECTRODE

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REDUCTION OF Co(II) COMPLEXES WITH SELECTED AMINO ACIDS ON A DROPPING MERCURY ELECTRODE

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The reduction of Co(II) complexes with amino acids Gly, Ala, Asn, Asp and Glu was studied polagographically. The species reduced on a mercury electrode and their electrochemical parameters were determined. It was shown that the first complex, in all studied systems, is reduced much easier, at less negative values of potentials than the aquaion. The stability constants of the complexes were also calculated. The effect of amino and carboxylate groups on the reduction mechanism of Co(II) complexes on a mercury electrode is discussed.

Keywords: Co(II) complexes; amino acids; polarography; reduction mechanism

INTRODUCTION

The reduction of Co(II) ions in the presence of ligands is rarely investigated by polarographic techniques. One of the reason is that Co(II) ions readily oxidised to Co(III) when bound to nitrogen donors.[1–2] Moreover, complexes of Co(II) formed at lower pH are reduced at potentials very close to the potential of hydrogenion reduction. Overlapping of Co(II) and hydrogen reduction waves makes quantitative analysis of the polarographic data very difficult or sometimes impossible.

Our earlier work on Co(II) complex reduction processes has shown that the metal ion, when bound to nitrogen donor(s), is reduced at more positive potentials than the aquaion.[3–5] This phenomenon is usually observed for Ni(II) complexes as well.

This paper presents data from a study of the reduction of Co(II) ions in the presence of potentially bidentate and terdentate ligands with nitrogen donors as main binding sites. Among the amino acids chosen only the glycine-Co(II) system has studied previously.[6] Our studies have shown that at low pH the reduction mechanism could be different than that proposed by Romia *et al.*[6] and it is reinterpreted below. The data obtained for other bidentate amino acids (Ala, Asn and Glu) support our interpretation of the low pH reduction mechanism proposed for the Co(II)-Gly system.

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 working electrode and a saturated calomel electrode as reference electrode. The mercury container was placed at a height of 45 cm, the mercury flowrate was 1.965 mg/s and the drop time was 4.04 s. A saturated calomel reference electrode was connected to the polarographic cell by a salt bridge filled with saturated sodium perchlorate. All measurements were performed at 25°C with an ionic strength of 0.5 mol dm^{-3} ($NaClO_4$). The concentration of Co(II) was fixed at 1 or 2×10^{-4} mol dm^{-3} 10 and the concentration of amino acids was varied from 1×10^{-4} to 5×10^{-2} mol dm^{-3}. All stock solutions were prepared with analytical reagent grade chemicals. Argon was bubbled through solutions to remove oxygen. Polyvinyl alcohol was used to suppress polarographic maxima in the Gly, Ala, Asn and Glu systems; pH was adjusted with NaOH or $HClO_4$.

RESULTS AND DISCUSSION

Co(II)-Glycine (Gly) system

Co(II) aquaions when reduced in 0.5 M $NaClO_4$ give a 2-electron, completely irreversible reduction wave at –1.2550 V. In the presence of Gly in the pH region 5–7, the single reduction wave is still observed, but it is shifted towards more positive potentials. Above pH 7 the reduction wave returns towards more negative reduction potential and splits into two waves. Although splitting is not very profound it is distinct enough to observe that one of the waves increases in height with pH while the other becomes smaller. At pH above 10.5 the major wave shifts again towards more positive potentials.

Logarithmic analysis of the first reduction wave (pH region 5–7) indicates that it consists of at least two reduction waves being at potentials very close to each other. Using the procedure proposed by Ruzic[7–8] both waves were successfully separated. Their slope coefficients were 103 and 44 mV and they correspond to the reduction of $Co(aq)^{2-}$ and CoL^+ (L = deprotonated Gly), respectively. The reduction wave which appears above pH 7 at potentials from −1.37 to −1.41 V with a slope coefficient of 59 mV can be assigned to the reduction of the CoL_2 complex.

In DPP three relatively well-resolved reduction peaks are observed. In the pH range 4.8–6.3 the peak at −1.320 V corresponding to aquaion reduction decreases, while that at −1.223 V corresponding to reduction of CoL^+ increases systetically. At pH 7 it reaches maximum height and above pH 7 it starts to decrease with a new peak growing at −1.40 V. The latter corresponds to reduction of CoL_2. The reduction peaks shown in Figure 1 clearly show that CoL^+ is reduced at about 97 mV more positive potentials than the aquaion. This differs from data reported earlier by Romia *et al.*[6] who suggested that the complex is reduced at potentials more negative than the aquaion. Figure 2 and 3 show the influence of pH and free ligand concentration on the variation of half-wave potential of Co(II) species and in Table I are collected values of E_p and slope coefficients for all species taking part in the reduction. The reduction wave observed at pH 7–10.5 is partly kinetic in character, while total current of both reduction waves observed at this pH range is diffusion in character. Thus, there is reaction in solution between the two electroactive species CoL^+ and CoL_4.

TABLE I Electrochemical parameters for different species reduced on the dropping mercury electrode in the Co(II)- amino acid systems.

	–Ep (V) (vs. SCE)			*2.3 RT/αn F (mV)*		
Amino acid	*M*	*ML*	*ML_2*	*M*	*ML*	*ML_2*
lGly	1.320	1.223	1.405	103	43–45	59
Ala	1.319	1.219	1.425	102	41–43	
Asn	1.320	1.215	1.386	103	41	59
Asp	1.320	1.291	1.667	102	59	59–60
Glu	1.319	1.249	1.543	101	44	62

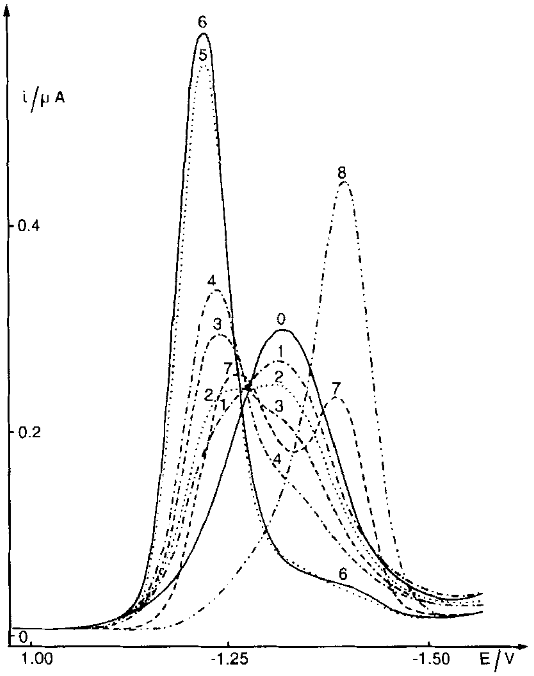

FIGURE 1 Differential pulse polagrams of Co(II) in the presence of Gly at different pH values in 0.5 M $NaClO_4$; Co(II) = 1×10^{-4} mol dm^{-3}; ΔE = 50 mV, tl = 1s; pH: 1) 5.30; 2) 5.40; 3) 5.56; 4)5.82; 5) 6.48; 6) 7.06; 7) 8.82; 8) 10.31.

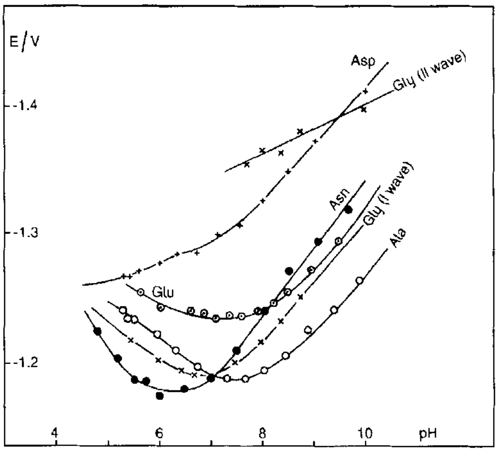

FIGURE 2 Influence of pH on the variation of half-wave potentials for reduction of Co(II) in the presence of amino acids.

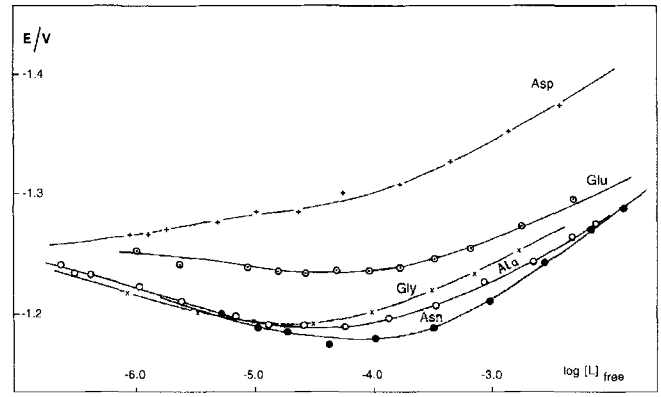

FIGURE 3 Effect of the concentration of freen amino acids in the variation of half-wave potentials for the reduction of Co(II).

Using the reduction wave equation given by Biernat and Baranawska-Zralko[9] stability constants for complexes and the electrode reaction rate constants were evaluated (Tables II and III). The hypothetical diffusion value for half-wave potential, ($E_{1/2\ \mathrm{diff}}$, for the kinetic reduction wave was evaluated similarly to that fot the reversible processes.[10] The formal difference consists in introducing the electron transfer coefficient, α, in the following expression.

$$(E_{1/2})_{\mathrm{diff}} = (E_{1/2})_{\mathrm{kin}} - RT/\alpha nF \ \ln i_d/i_k$$

The rate constant for the dissociation $CoL_2 \rightarrow CoL^+ + L^-$, k_{21}, was calculated from the equation for the kinetically controlled current[11] : $i_k/(i_d - i_k) = 0.886(\rho t1/\sigma)_{1/2}$ where;

$$\rho = k_{21}\ \beta_2 L^2 / (\beta^2 L^2 + \beta_3 L^3$$
$$\sigma = (\beta_2 L^2 + \beta_3 L^3) / (1 + \beta_1 L)$$

and the value obtained for k_{21} was 35.4 s^{-1}.

The results obtained for the Co(II)-Gly system suggest the following scheme for the reduction.

$$\begin{tikzcd}
\mathbf{Co(ac)^{2+}} \arrow[r, leftrightarrow] \arrow[d, "\alpha_0\ k^0(Co(aq)^{2+})"] & \mathbf{CoL^+} \arrow[r, leftrightarrow, "k_{12}"] \arrow[d, "\alpha_1\ k_{21}\ k^0(CoL^+)"] & \mathbf{CoL_2} \arrow[r, leftrightarrow, "fast"] \arrow[d, "\alpha_2\ k^0(CoL_2)"] & \mathbf{CoL_3^-} \\
\mathbf{Co(Hg)} & \mathbf{Co(Hg)} & \mathbf{Co(Hg)} &
\end{tikzcd}$$

wave I **wave II**

Co(II)-α-Alanine (Ala) system

The polarographic behaviour of this system is very similar to that of Co(II)-Gly and the stability constants as well as the electrokinetical parameters were calculated as described above for the Co(II)-Gly system. The values obtained are collected in Tables I to III. DPP polarograms exhibit three peaks and clearly show that CoL^+ is reduced easier (by 100 mV) than the aquaion Table I.

TABLE II Values of electrode reaction rate constants and dissociation rate constants for different species in the studied systems.

Amino acid	$i_d^{Co(II)}$ / μA	$i_{Co(II)}$ / *mM*	c_{PVA} / %	$D_{Co^{2+}}{}^{II} \times 10^6$ cm^2/s	$k_{Co(aq)^{2+}}$ / *cm/s*	k_{CoL} / *cm/s*	k_{CoL2} / *cm/s*	k_{21} / s^{-1}
Gly	1.428	0.2	0.004	8.6019	1.65×10^{-3}	8.23×10^{-2}		35.40
Ala	0.720	0.1	0.002	8.7474	1.66×10^{-3}	1.16×10^{-1}		159.67
Asn	1.428	0.2	0.004	8.6019	1.65×10^{-3}	2.06×10^{-1}	5.93×10^{-3}	
Asp	1.374	0.2	0	7.9637	1.50×10^{-3}	5.25×10^{-4}		6.15
Glu	1.422	0.2	0.004	8.5299	1.64×10^{-3}	7.54×10^{-4}		142.75

$E_{1/2}{}^{Co(II)} = -1.2550$ V.

TABLE III Proton dissociation constants for amino acids studied and stability constants for their complexes with Co(II).

Amino Acid	$pK_{a\text{-}COOH}$	$PK_{side\ chain}$	pK_{NH3^+}	$log\beta_{ML}$	$log\beta_{ML2}$	$log\beta_{ML3}$	*Method*	*Ref*
Gly	2.47		9.76	4.66	8.53		gl	19
				4.65	8.43	10.81	gl	20
				5.5	9.0	11.3	elph	21
				4.51	8.16	10.45	gl	22
				5.07	8.99	12.40	gl	24
				4.77	8.99	12.40	gl	24
				5.00	9.25	11.30	pol	this work
Ala	2.45		9.90	4.27	7.72	9.47	gl	20
				5.0	8.2	10.6	elph	21
				4.82	8.48		sol	25
				4.70	8.75	10.82	pol	this work
Asn	2.09		8.79	4.55	8.13	9.96	gl	20
			4.45	7.99		gl	26	
				4.903	9.029	11.855	pot+cal	27
				4.50	8.10	1135	pol	this work
Asp	1.94	3.70	9.62	5.90	10.18		gl	19
				5.94	10.23		gl	26
				5.75	9.70		pol	this work
Glu	2.19	4.28	9.95	4.9	8.0		elph	21
				4.56	7.86		gl	26
				4.55	8.25		pol	this work

Co(II)-L-Asparagine (Asn) system

In the presence of Asn only one reduction wave for Co(II) is observed over the whole pH range studied. This shifts towards more positive potentials when the aquaion reacts to give CoL^+ (pH 5.0–6.5) and towards more negative values at pH above 7 when CoL_2 is formed. Logarithmic analysis of the reduction waves obtained for this system indicate the simultaneous reduction of several species.[7–8] At lower pH (below 7) the aquaion and CoL^+ species are reduced, while above 7 CoL^+ and CoL_2 are reduced simultaneously.

The slope obtained for the plot of $\Delta E_{1/2}$ *vs*-log[Asn^-] at high ligand concentrations indicates that the major form in solution and the species reduced at the electrode differ in average ligand number[12] by value of 1.32. Since in this concentration range under the conditions used the major species reduced are CoL^+ and CoL_2 (Figure 4) and the amount of CoL_2 is rather low, the presence of CoL_3^- in solution is suggested. The diffusion character of all reduction waves indicate that equilibrium between all in solution is reached relatively quickly.

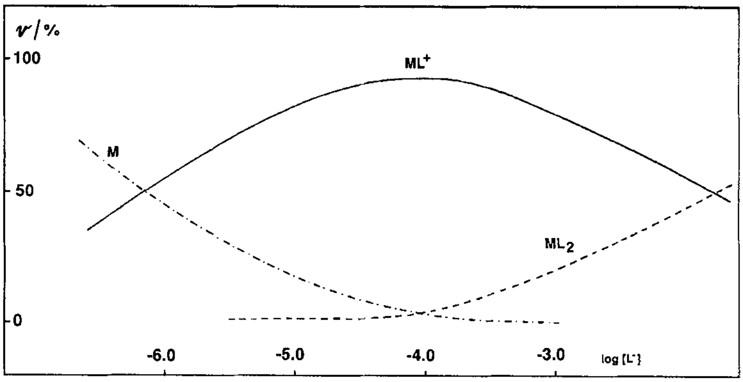

FIGURE 4 Contributions of different species to the rate (v) of the total electrode reaction in the Co(II)-Asn system.

Values of stability constants and electrochemical parameters were obtained by the same methods as those for the Co(II)-Gly system. Contributions of particular species to the rate of the electrode reaction are shown in Figure 4 and the half-wave potential variations *vs* log[Asn^-] calculated from these contributions are shown in Figure 5.

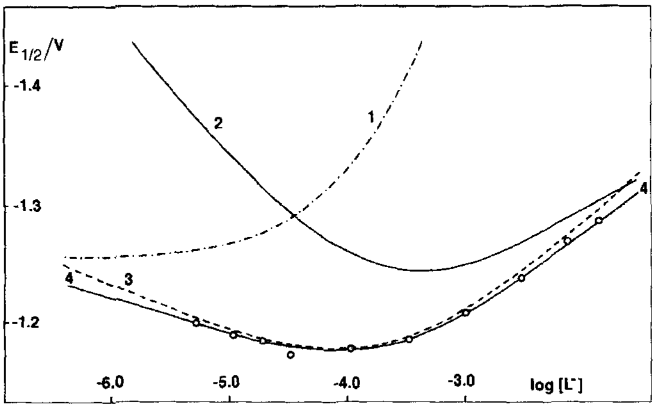

FIGURE 5 Possible changes in half-wave potentials assuming that the reduction of Co(II)-Asn complexes proceeds (1) by the Co(II) aquaion only, (2) by the Co(Asn)$^+$ 8 complex only, (3) by the Co(Asn)$_2$ complex only; (4) are experimental half-wave potentials during simultaneous reduction by all species.

Co(II)-L-Aspartic acid (Asp) system

The behaviour of Co(II) ions in the presence of potentially terdentate Asp is slightly but distinctly different to that described above for bidentate ligands. The reduction wave for Co(II) practically does not change potential in the pH range 5.0–5.9, although it becomes distinctly more reversible. Above pH 6.0 the reduction wave starts to move towards more negative values, decreasing its limiting current. Simultaneously, at –1.60 V, the other reduction wave appears and increases its limiting current. In very basic solutions the third wave appears at –1.37 V.

The lower pH reduction wave (pH 5.0–5.9) comprises two reduction processes (aquaion and CoL). Both species are reduced at very close potentials and even in DPP polarograms only one reduction peak is observed (Figure 6). At pH around 6.0, however, the DPP reduction peak represents mostly the reduction of CoL and it is shifted by 30 mV towards more positive values when compared to the aquaion (Table I). From logarithmic analysis of the waves obtained below pH 6 the slope coefficients of 102 and 59 mV were evaluated for Co(aq)$^{2+}$ and CoL species, respectively. The slope coefficient of the reduction wave at –1.60 V is the same as for CoL, *i.e.*, 59 mV. The reduction wave observed above pH 7.0 is kinetic in character but the total reduction wave keeps its diffusion character. This indicates slower kinetics in the equilibrium reaction $CoL_2^{2-} \rightleftharpoons CoL + L^{2-}$. The rate constant of this reaction was calculated according to equation[11] $i_k/(i_d - i_k) = 0.886(\rho t_l/\sigma)^{1/2}$
where $\sigma = \beta_2 L^2/(1 + \beta_1 L)$ and $\rho = k_{21}$;
k_{21} is 6.15^{S-1}.

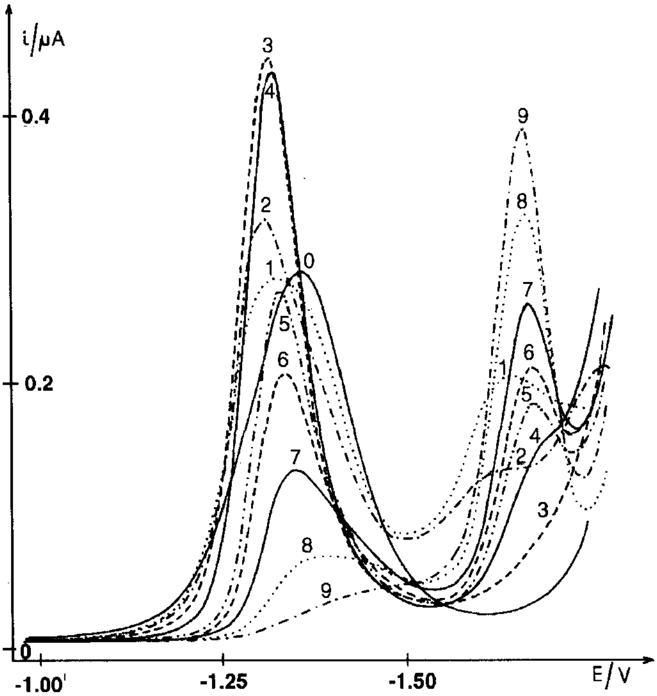

FIGURE 6 Differential pulse polarograms of Co(II) in the presence of Asp at different pH values in 0.5 M $NaClO_4$; Co(II) = 1×10^{-4} mol/dm^{-3}, Asp = 1×10^{-2} mo dm^{-3}; $\Delta E = 50$mV, t_1=1s; pH: 1) 5.10; 2) 5.44; 3) 5.87; 4) 6.13; 5) 7.20; 6) 7.71; 7) 8.21; 8) 9.31; 9) 10.18.

Co(II)-L-Glutamic acid (Glu) system

Glu is potentially a terdentate ligand. However, the thermodynamically unfavourable formation of a 7-membered chelate ring usually excludes the γ-carboxylate group of Glu from simultaneous metal ion coordination. Thus, as expected, the polarographic behaviour of the Co(II)-Glu system was similar to that of the bidentate amino acids. Reduction of CoL occurs at potentials less negative than that of the aquaion. At pH 8, where the major complex is CoL_2^{2-}; the DC reduction wave is observed at −1.54 V. This vanishes in strongly alkaline solutions due, most likely, to the formation of the electrochemically inactive CoL_3^{4-} species.

The polarographic data indicate that Co(II) forms three distinct species with Gly, Ala and Asn, two complexes with Asp and three species with Glu. In this group of amino acids three are potentially terdentate, Asp, Asn and Glu. Asp binds metal ions *via* NH_2, α-COO^- and β-COO^- groups. However, Asn and Glu seem to act only as bidentates. It should be mentioned that an earlier potentiometric study suggested that in Co(II) complexes with Asn and Glu, considerable amounts of the terdentates are formed, 74, 51 and 98% for Asn, Glu and Asp, respectively.[13]

Equilibrium between different species in the studied solutions was found to be quickly established only in the case of the Co(II)-Asn system, while in all other cases the limiting currents of the reduction waves are kinetically controlled, suggesting that equilibrium between CoL^+ and CoL_2 complexes is relatively slow. Rate constants for CoL_2 dissociation to CoL obtained are collected in Table II.

In the systems studied the first complex reduced at more positive values than the aquaion. This difference is from 105 mV for Asn to 29 mV for Asp and the phenomenon seems to be typical of Co(II) ion complexes; the same positive shift was observed also for ammonia as well as aminosugar complexes.[3-5] Comparison of all complexes indicates that the carboxylate group strongly diminishes this positive shift caused by coordination of the nitrogen donors. The presence of the second carboxylate group (Glu, Asp), especially when it is bound to the metal ion (Asp), makes complex reduction even more difficult (Table I). In the case of dicarboxylic acids the first complex formed is reduced at potentials more negative than the aquaion.[14-15] The amide group in the Asn side chain, on the other hand, causes the most positive effective shift for CoL. The same effects for amino acids complexes were observed for Ni(II)[16]. It is noteworthy that the positively charged amino groups when present in the ligand bound *via* glycine-type coordination to Co(II) ions, *e.g.*, in 2, 3-diaminopropionic and 2, 4-diaminobutyric acids[17] makes CoL complex reduction still easier.[18] The carboxylate groups also affect the reduction of CoL_2. The CoL_2 complexes of Asp, then Glu are reduced more easily that these of Ala, Gly and Asn (Table I).

Stability Constants

Stability constants for particular complexes were evaluated from polarographic data and are compared in Table III with those obtained by other methods. Although polarography is not the most efficient method for evaluating precise values of stability constants, the data collected in Table III are in good agreement with those obtained from potentiometric titration. It should be mentioned here that various sets of stability constants obtained by potentiometry may differ considerably (see, *e.g.*, the Co(II)-Gly system.[28] The major error (~ 0.03 log units) derives from the precision of the reduction potential (~ 0.5 mV). These also depend on changes of diffusion coefficients resulting from complexation. They can usually be corrected to some extent by the term $RT/(\alpha nF) \bullet \ln(i_{ds}/i_{dc})$, where i_{ds} and i_{dc} are the limiting currents of the ligand free and complex metal, respectively. An additional problem is introduced by simultaneous reduction of more than one complex on the electrode with badly resolved reduction waves.

However, the stability constants obtained here seem to be reasonable. The waves log (K_{CoL}/K_{CoL2}) obtained for Gly and Ala are close to 0.7, the value predicted by statistics for bis-complexes of bidentate ligands in octahedral complexes.[13] This is very high for Asp, 1.8, due to terdentate ligand coordination. For Asn and Glu, the values are 0.90 and 0.85, respectively. This may suggest some involvement of amino acid side chain in metal ion coordination but of minor importance.

Acknowledgments

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