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Cadmium Succinate and Cadmium Malate Stability Constants Revisited

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The complexes formed in the cadmium(II) succinate (suc^{2-}) hydrogen ion and in the cadmium(II) malate (mal^{2-}) hydrogen ion systems in aqueous solution at 37 °C and $I = 150$ mmol·dm^{-3} (NaCl) have been characterized by means of glass-electrode potentiometry. The succinate and malate protonation constants were found to be 5.187 ± 0.001, 9.135 ± 0.002 and 4.618 ± 0.001, 7.804 ± 0.002, respectively. The formation constants for the complexes Cdsuc, $CdsucH^+$, and Cdmal were found to be 1.63 ± 0.02, 6.26 ± 0.06, and 1.25 ± 0.05, respectively. Particular attention has been paid to the evaluation of the effect of possible systematic errors on the constant values determined. Reliable standard deviation estimations have been made by applying a Monte Carlo calculation technique. Cyclic voltammograms and differential pulse polarograms for both cadmium(II) systems were consistent with formation of weak, labile complexes.

Introduction

Succinic acid (butanedioic acid, ethane dicarboxylic acid), $HOOC-CH_2-CH_2-COOH$, and malic acid (hydroxybutanedioic acid, monohydroxysuccinic acid), $HOOC-CHOH-CH_2-COOH$, are naturally occurring ligands present in many organisms. Succinic acid is an important intermediate in the tricarboxylic acid cycle, where it is formed from α-ketoglutaric acid. It is used via reactions in the tricarboxylic cycle and in the glyoxylate cycle for the synthesis of amino acids and carbohydrates. The S-isomer of malic acid is also an intermediate both in the tricarboxylic acid cycle, being formed by hydration of fumaric acid and converted into oxaloacetic acid by malate deshydrogenase, and in the glyoxylate cycle. Succinate is present, in free or bound form, especially as calcium and potassium succinates, in unripe fruits, algae, fungi, and lichens. Malate plays several metabolic roles in plants, for example in the diurnal acid rhythm of the *Crassulaceae*. Malic acid is found free in sour apples, quinces, and berries. Succinate and malate are used in the preparation of drugs and in flavorings. Malic acid is also used to impregnate packing materials for foods.

Despite their biological significance, values of the stability constants for metal succinate and malate systems in aqueous solution have rarely been determined under conditions of temperature and ionic strength close to those relevant for biological fluids.

Determination of stability constants for weak complexes, as in the present case for the cadmium succinate and malate systems, is not straightforward because the analytical signals are only slightly perturbed in the presence of complex formation. This situation is common to many biological, and environmental, systems. For such systems, the effect of experimental errors on model selection and on the constant values obtained can be very important and must be carefully checked. Failure to adequately consider these aspects may be a source of the disparity among published stability constant values.

In the present study, two different analytical techniques are applied, glass potentiometry and voltammetry. Particular attention is paid to the evaluation of the effect of possible systematic errors on the constant values determined, and reliable standard deviation estimations are made by applying a Monte Carlo calculation technique. Comparison of the values obtained with previously published values allows discussion of the validity and limitations of some of the existing values.

Experimental Section

Potentiometric Studies. A. Reagents. Analytical grade reagents were used throughout. All solutions were prepared using demineralized water (Millipore system), which had been boiled and cooled under nitrogen, and stored under an atmosphere of purified nitrogen.

Malic and succinic acids were purchased from Merck. They were potentiometrically assayed and found to be sufficiently reliable to be used without further purification. Ligand solutions were freshly prepared daily by direct weighing.

Stock solutions of cadmium were prepared from their chloride salts and were made slightly acidic by adding

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hydrochloric acid to prevent hydrolysis and adsorption of carbon dioxide. The metal content of the solutions was determined against EDTA using xylenol orange as indicator (Vogel, 1971). Their mineral acid content was determined by titration with standard alkali (Gran, 1988) and the concentration verified by using the MAGEC program (May et al., 1982).

Carbonate-free sodium hydroxide solutions were prepared from Merck standard volumetric solutions. Alkali titer and absence of carbonate were checked by means of Gran plots (Gran, 1988) using potassium hydrogen phthalate (Merck) as the acid.

B. Technique and Experimental Conditions. Formation constants were determined from potentiometric titrations. A Radiometer PHM93 millivoltmeter was used to monitor the emf of cells of the type

$$\text{G.E.}|\text{Cd}^{2+}, \text{ligand}, \text{H}^{+}, \text{NaCl (150 mmol}\cdot\text{dm}^{-3})|\text{R.E.}$$

where G.E. denotes a glass electrode (Orion 91-01) and R.E. a double-junction silver/silver chloride reference electrode (Orion 90-02). Successive aliquots of sodium hydroxide were added to the solution by means of a Metrohm Multidosimat 665 autoburet. A versatile computer-controlled system for data acquisition was used throughout. All experiments were carried out in a titration cell thermostated at (37 ± 0.02) °C by circulating thermostated water. Titrations were performed in a nitrogen atmosphere.

Sodium chloride (150 mmol·dm^{-3}) was used to maintain the ionic strength constant and to ensure isotonicity with blood plasma. Although, from the thermodynamic viewpoint, the conditions used are not ideal due to the possible association of chloride with metal ions (Daniele et al., 1985), the advantage is that constants obtained in this salt solution implicitly account for the influence of the biological medium.

The electrode system was calibrated in terms of hydrogen ion concentrations by performing strong acid versus strong base titrations (Linder et al., 1984). The logarithm of the concentration quotient for water dissociation under the same experimental conditions was found to be −13.36, in good agreement with literature values (Pettit and Powell, 1997).

The cadmium and ligand solutions used were acidified such that all the ligand donor groups were protonated at the beginning of each titration. Titrations were performed over the wider range of metal-to-ligand ratios allowed by the working ionic strength. Data were recorded over the widest possible −log[H] range. Replicate titrations were done to check reproducibility.

Titration data used for calculating formation constants are summarized in Table 1.

Table 1. Summary of Titration Data Used in the Formation Constant Calculations: Number of Titration Points, Initial Total Concentrations of Cadmium(II) (T_M), and Ligand (T_L) in mmol·dm^{-3}, and −log[H] Range Investigated

system	titration	no. of points	T_M	T_L	−log[H] range
suc-H$^+$	1	48		5.1	2.30−8.50
	2	46		5.1	2.30−6.06
	3	50		9.6	2.29−6.54
	4	50		9.6	2.29−6.55
	5	48		14.9	2.28−6.49
	6	49		14.9	2.28−8.67
	7	45		15.39	2.28−6.95
	8	59		15.39	2.29−6.52
	9	53		19.25	2.28−6.22
	10	53		19.25	2.28−6.22
	11	55		19.86	2.28−6.37
	12	47		19.86	2.28−6.37
mal-H$^+$	1	45		4.85	2.27−5.62
	2	46		4.85	2.27−6.16
	3	44		5.17	2.26−5.07
	4	48		5.17	2.27−6.32
	5	42		10.08	2.24−6.08
	6	52		10.08	2.23−5.97
	7	53		10.34	2.23−5.93
	8	57		14.94	2.21−5.76
	9	43		14.94	2.20−5.75
	10	63		19.98	2.18−7.02
	11	56		19.98	2.18−6.04
Cd^{2+}-suc-H$^+$	1	42	0.8554	12.36	2.79−5.37
	2	42	0.8554	12.36	2.79−5.37
	3	43	0.8554	16.29	2.74−5.50
	4	42	0.8554	17.30	2.74−5.28
	5	41	0.8554	17.30	2.73−5.23
	6	51	0.8554	26.21	2.68−6.01
	7	52	0.8554	26.21	2.68−6.18
	8	44	1.711	7.616	2.68−5.50
	9	51	1.711	17.40	2.61−5.84
	10	49	1.711	17.40	2.61−5.65
	11	49	1.711	26.03	2.56−5.73
	12	49	1.711	26.03	2.57−5.74
	13	52	3.421	7.62	2.44−5.79
	14	50	3.421	26.03	2.39−5.67
Cd^{2+}-mal-H$^+$	1	50	0.8554	16.17	2.46−5.95
	2	45	0.8554	17.06	2.46−4.93
	3	43	1.711	7.33	2.52−4.97
	4	47	1.711	17.06	2.40−4.99
	5	47	1.711	17.06	2.70−4.99
	6	52	1.711	17.54	2.39−5.33
	7	55	1.711	17.4	2.39−5.91
	8	48	1.711	25.70	2.32−5.13
	9	46	1.711	25.70	2.31−4.96
	10	51	3.421	7.33	2.38−5.28
	11	52	3.421	17.37	2.28−5.14
	12	53	3.421	17.37	2.29−5.23
	13	54	3.421	25.70	2.24−5.71

***C.* Calculation Procedures.** The general equilibria involving metal M^{2+}, ligand L^{2-} (i.e. deprotonated succinic acid = suc, deprotonated malic acid = mal), and H$^+$ ions can be written as

$$p\text{M} + q\text{L} + r\text{H} \rightleftharpoons \text{M}_p\text{L}_q\text{H}_r \tag{1}$$

Signs are omitted for simplicity. The overall formation constant is denoted by β_{pqr}.

The titration data were processed with the ESTA computer program library (May et al., 1985, 1988; May and Murray, 1988a, 1988b) by following our previously described approach (Filella et al., 1987a, 1987b; García Bugarín et al., 1989; García-Tasende et al., 1991a, 1991b) involving optimization and simulation in successive steps. The initial models were obtained from the experimental protonation, deprotonation and formation curves. Protonation curves are obtained by plotting the average number of protons bound to each ligand, $\bar{Z}_H$, as a function of −log[H]

$$\bar{Z}_\text{H} = \frac{T_\text{H} + nT_\text{L} - T_\text{OH} + [\text{OH}] - [\text{H}]}{T_\text{L}} \tag{2}$$

where T_H, T_L and T_{OH} = total concentrations of strong acid, ligand, and hydroxide, respectively and n = number of titratable protons of the ligand. Deprotonation curves are obtained by plotting $\bar{Q}$ as a function of −log[H], $\bar{Q}$ being defined as

$$\bar{Q} = \frac{T^*_\text{H} - T_\text{H}}{T_\text{M}} \tag{3}$$

Table 2. Formation Constants, β_{pqr}, Determined in This Study at 37 °C and $I = 150$ mmol·dm^{-3} NaCl ($\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$)

system		p q r	log β_{pqr}	SD[a]	OF[b]	R[c]	n[d]
suc-H$^+$	OBJT	0 1 1	5.1772	0.0002	4.14E−10	0.001	611
		0 1 2	9.1268	0.0002			
	OBJE	0 1 1	5.1787	0.0002	0.58	0.002	
		0 1 2	9.1283	0.0002			
	DHC[e]	0 1 1	5.1875	0.0002	0.62	0.002	
		0 1 2	9.1360	0.0003			
	best values[f]	**0 1 1**	**5.187**	**0.001**	**0.25**		
		0 1 2	**9.135**	**0.002**			
mal-H$^+$	OBJT	0 1 1	4.6108	0.0002	4.07E−10	0.001	549
		0 1 2	7.7971	0.0002			
	OBJE	0 1 1	4.6109	0.0002	0.366	0.001	
		0 1 2	7.7976	0.0002			
	DHC[e]	0 1 1	4.6183	0.0002	0.282	0.001	
		0 1 2	7.8043	0.0002			
	best values[f]	**0 1 1**	**4.618**	**0.001**	**0.31**		
		0 1 2	**7.804**	**0.002**			
Cd^{2+}-suc-H$^+$	OBJT	1 1 0	1.669	0.005	1.07E−09	0.001	657
		1 1 1	6.293	0.010			
	OBJE	1 1 0	1.662	0.006	0.77	0.002	
		1 1 1	6.298	0.012			
	DHC[e]	1 1 0	1.630	0.006	0.62	0.002	
		1 1 1	6.259	0.012			
	best values[f]	**1 1 0**	**1.63**	**0.02**	**0.01**		
		1 1 1	**6.26**	**0.06**			
Cd^{2+}- mal-H$^+$	OBJT	1 1 0	1.328	0.010	2.35E−09	0.002	643
	OBJE	1 1 0	1.331	0.010	1.49	0.002	
	DHC[e]	1 1 0	1.244	0.011	1.48	0.002	
	best values[f]	**1 1 0**	**1.25**	**0.05**	**0.01**		

[a] Standard deviations as given by the program. [b] OF, in OBJE output = $[\Sigma w(\mathrm{EMF}_i^{o} - \mathrm{EMF}_i^{c})^2]/(N - n_p)$; in OBJT output = $[(T_i^{o} - T_i^{c})^2]/(N - n_p)$, where N = number of points, n_p = number of refined parameters, and T_i = total concentrations. See the Calculation Procedure section for an explanation of why both OBJT and OBJE results are given. [c] R = Hamilton R factor. [d] Number of points used in the calculations. [e] Values corrected for variations in ionic strength along the titrations as described in the text (weighted OBJE option with Debye−Hückel corrections applied). [f] Formation constants calculated by applying the Monte Carlo technique described in the text (number of Monte Carlo cycles = 99). The OBJE weighted optimization option with correction for variations in ionic strength along the titrations has been used.

where T_H^* is the calculated total concentration of protons in the system at the observed −log[H]. Metal complex formation curves show the variation of the average number of ligands bound per metal ion $\bar{Z}_M$, as a function of −log[A]

$$\bar{Z}_M = \frac{T_L - [A](1 + \sum_n \beta_{LH_n}[H]^n)}{T_M} \qquad (4)$$

where

$$[A] = \frac{T_H - [H] + [OH]}{\sum_n n\beta_{LH_n}[H]^n}$$

and T_M = total metal concentration.

The shapes of these curves were used to predict the stoichiometry of the possible complexes present in the system as well as to obtain rough estimates for their formation constants. Formation constants were estimated initially by using the BETA task of ESTA (May et al., 1988). This task calculates the formation constant values for a single species from the emf reading at each titration point by assuming that this is the only species formed. Model selection was based on five criteria: (i) search for the minimum value of the objective function being minimized, (ii) good internal consistency of the data as reflected by small standard deviations of formation constants, (iii) best fit between experimental and calculated graphical visualizations of the data (protonation and formation curves) for the different models tested, (iv) calculation of the degree of formation of each species (complexes not reaching 10% of the total metal concentration over a range of points in more than one titration were regarded as dubious), and (v) application of chemical common sense.

Formation constants were refined by using the ESTA optimization module (May et al., 1988). The ESTA objective function can be minimized with respect to either total ion concentrations (OBJT) or emf (OBJE). The objective function based on unit-weighted residuals in total analytical concentrations (OBJT) was used throughout the model selection procedures. Optimization of the “best” set of species was performed by applying the weighting scheme proposed by May and Murray (1988a) on the emf-based objective function. The weight at each titration point was based on errors of 0.2% in analytical concentrations, 0.005 cm^3 in titer and 0.05 mV in emf. Results based on unweighted total ion concentration residuals (OBJT) and on weighted emf residuals (OBJE) are given in Table 2. OBJE results should be considered as being the “best” set of constants, but it should be borne in mind that weighted functions are not directly comparable among different chemical systems because they depend on estimates of errors and on how the weighting is done. It is because of this that unweighted OBJT values are also given.

Ionic strength may vary to some extent over the course of a titration when the background supporting electrolyte is maintained constant at relatively low concentrations, as is the case in the present study. The ESTA computer program library allows the data to be corrected for this factor by calculating ionic strength values at each titration point (May et al., 1985). This correction is based on the extended Debye−Hückel equation for the calculation of the activity coefficient for each component and complex. When the Debye−Hückel parameters for all components and complexes are not introduced, default values implemented in the ESTA computer program library are used (Linder and Murray, 1982). All complexes and anionic components appearing in complexes are assumed to be small organic ions and the other component ions are considered to be inorganic. Hydrogen and hydroxide ions are treated as special cases (ionic size parameters are 9.0 and 3.5, respectively, and $c = -0.06$ for both).

The effect of interfering ions in the electrode response may be significant, particularly at high pH values. In the case of glass electrodes, the behavior observed in the presence of one univalent interfering ion can be described by the Eisenman equation (Eisenman, 1962; May et al., 1985)

$$E_k^{\mathrm{IS}} = s_k \log(\{X_k\}^{1/\alpha} + K_{ki}\{X_i\}^{1/\alpha})^{\alpha} \qquad (5)$$

where E_k^{IS} = electrode potential, s_k = electrode response slope, $\{X_i\}$ = free concentration of component i, and α and K_{ki} (K_{ki} = selectivity coefficient of component i) are empirical parameters. The computer program ESTA uses this approach (May et al., 1988).

The Henderson equation (Henderson, 1907) predicts potentials across junctions of different univalent electrolytes at constant ionic strength from ionic conductances of species present in the test and in the bridge solutions. Despite the fact that saturated potassium chloride bridges violate one of the hypotheses of Henderson's equation (constancy of activity coefficients across the junction), this equation has been applied to such bridges (Bates, 1981; May et al., 1985) and is used here.

The ESTA computer program library allows the calculation of realistic standard deviations for the formation constants by using a Monte Carlo procedure (May and Murray, 1988b). It is implemented as follows. In every Monte Carlo cycle, a new set of randomly generated errors is imposed on those parameters which are to be held constant in the subsequent optimization. A simulation is then performed in which the emf at each point is determined on the basis of the perturbed titration-parameter values. A further error, based on the standard deviation of the emf readings, is randomly generated and imposed on this calculated emf. Finally, the formation constants are optimized with the simulated error-loaded data. If the optimization is successful, the resulting values are stored for subsequent averaging over all Monte Carlo cycles and evaluation of the corresponding standard deviations. In this work, 99 Monte Carlo cycles were used in determining the standard deviations reported.

Voltammetric Studies. A. Reagents. All solutions were prepared in deionized water (resistance 18 MΩ). A cadmium stock solution was prepared from $Cd(NO_3)_2 \cdot 4H_2O$ (Fluka, puriss, p.a.). $NaClO_4$ was from Fluka (puriss, p.a.). Boric acid buffer (pH 8.2) was prepared from 5 mmol·dm^{-3} H_3BO_3 (Fluka, puriss, p.a.) and 0.5 mmol·dm^{-3} carbonate-free NaOH (Prolabo, AR).

B. Technique and Experimental Conditions. An Ecochemie Autolab PGSTAT10 potentiostat was used in conjunction with a Metrohm 663 VA stand. The working electrode was a Metrohm multimode mercury drop electrode (mercury drop surface area 0.52 mm^2; Aldrich, ACS reagent mercury, 99.9995%), the auxiliary electrode was glassy carbon, and the reference electrode was Ag/AgCl/Cl$^-$ (sat.) encased in a 100 mmol·dm^{-3} KNO_3 jacket.

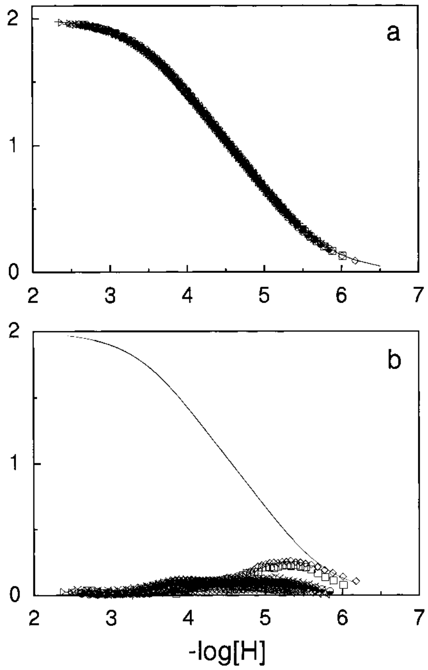

Figure 1. Experimental protonation (a) and deprotonation (b) curves for the Cd^{2+}-suc-H$^+$ system. Different symbols refer to different titrations. The theoretical protonation curve for the ligand in the absence of metal is shown as a solid line.

For cyclic voltammetry, scan rates in the range 200 mV/s to 20 V/s were used. For differential pulse polarography (DPP) the specific parameters were as follows: modulation time, 0.05 s; interval time, 2 s; modulation amplitude, 0.05 s; step potential, 0.004 V.

Measurements were performed at pH 8.2 in boric acid buffer, 150 mmol·dm^{-3} $NaClO_4$. All solutions were purged with oxygen-free nitrogen prior to analysis (and following addition of any spikes), and a positive nitrogen pressure was maintained over the solutions during measurement.

Results and Discussion

Potentiometric Studies. The values calculated for the formation constants are shown in Table 2.

A. suc-H$^+$ and mal-H$^+$ Systems. The systems suc-H$^+$ and mal-H$^+$ were studied by performing 12 and 11 titrations, respectively, with initial ligand concentrations varying in the range 5−20 mmol·dm^{-3}. In both cases protonation curves consisted of only one buffer zone. Both ligands contain two dissociable carboxylic protons which ionize simultaneously. The experimental data reported completely cover the dissociation of both protons. The hydroxyl group present in the malic acid molecule will dissociate at pH ≈ 17, according to the Taft equation (Perrin et al., 1981), thus far beyond the experimentally measurable pH range. Malic acid shows pK values more acidic than those for succinic acid because of the inductive influence of the hydroxyl group present in the molecule. Malate protonation constants are close to those measured for the carboxylic groups of mercaptosuccinic acid (Filella et al., 1986).

B. Cd^{2+}-suc-H$^+$ System. The Cd^{2+}-suc-H$^+$ system was studied by performing 14 titrations. The individual metal complex formation curves at different M/L ratios did not overlap; thus suggesting the formation of complexes other than ML. Some curves were ill-defined at the end of the titrations. The maximum $\bar{Z}_M$ values found rarely exceeded 0.5. Protonation and deprotonation curves (Figure 1) showed that metal complexes begin to form at approximately −log[H] = 2, that is, when the ligand starts losing

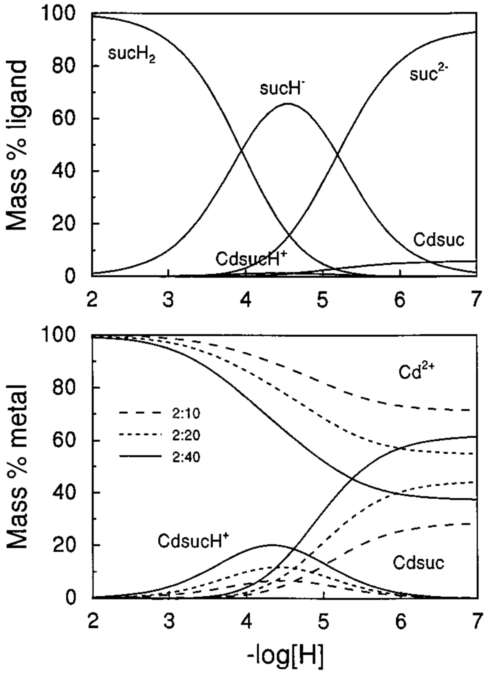

Figure 2. Ligand and metal species distribution as a function of −log[H] for different Cd(II) and succinate ratios. M/L concentrations (in mmol·dm^{-3}) are indicated in the figures.

its first proton, thus implying that for coordination to take place in solution the ionization of at least one carboxylate group is necessary. As shown in Figure 1a, the shift of the experimental ligand protonation curves in the presence of metal with respect to the theoretical curve for the ligand in the absence of metal is very small, thus indicating that the complexation of cadmium by succinate is weak (consistent with the voltammetric studies).

Using our approach, which includes optimization and simulation in successive steps, 12 complexes and >20 models were tested in order to obtain the "best" model. The ML complex was found to be the major species present under all the conditions investigated. As the formation curves were not fully superimposable, the presence of the complex MLH was also considered. This significantly improved the goodness-of-fit parameters, MLH accounting for approximately 15% of Cd^{2+} in the higher ligand-to-metal ratio experiments (the percentage of MLH formation ranges from 5% in titration 13 to 14% in titrations 6, 7, 11, 12 and 14). No formation of the ML_2 complex seems to occur under our titration conditions, and no value for its formation constant could be calculated. Constant values for other minor species were calculated by the program, but their inclusion in the model did not improve the goodness-of-fit and the estimated error for the calculated value for their constants was very high. Moreover, speciation calculations showed that these species, if present, would represent less than 2% of the total metal concentration in any titration. Although a certain (small) degree of formation of some minor species cannot be completely discarded, they were not included in the final model because their very weak formation does not allow the calculation of reliable values for their formation constants. Moreover, they probably are fitting artifacts. The model finally chosen, including ML and MLH, resulted in a satisfactory numerical and graphical fitting, considering the weak complexation equilibria studied. Metal and ligand species distribution as a function of −log[H] is shown in Figure 2 for different metal-to-ligand ratios.

Cadmium−succinate equilibria have been the object of a certain number of studies. Published values are found in Table 3. Log *K* values for the ML complex range from 0.66 to 2.81. Our model compares best with a study published 36 years ago (Schwarzenbach and Szilard, 1962). A close look at more recently published data shows that most of the authors include the same set of constants ML_l, ML_2, and ML_3. However, no evidence for the existence of these species is given, nor are there any indications that alternative complexation models were considered (and rejected). Moreover, most of the papers provide no details of the experimental methods used or of the data treatment procedures employed. Some of these values have been included in databases (SC-Database (Pettit and Powell, 1997), where the paper by Schwarzenbach and Szilard is not included) and, presumably, used by other scientists. Unfortunately, this is not an isolated case. Considerable discrepancies among values published for the same chemical system by different authors is a notorious feature of formation constant measurement and may be especially important for weakly complexing systems. This issue is discussed further in the Error Treatment section.

C. Cd^{2+}-mal-H^+ System. The Cd^{2+}-mal-H^+ system was studied by performing 13 titrations. The maximum $\bar{Z}_M$ values found rarely exceeded 0.5. The shift of the experimental ligand protonation curves (Figure 3a) in the presence of metal with respect to the theoretical curve for the ligand in the absence of metal as well as the corresponding deprotonation curves (Figure 3b) indicate a weak complexation of the cation by malate. Again, 12 complexes and >20 models were tested in order to obtain the "best" model. The only complex for which a reliable constant value could be calculated was ML. Metal and ligand species distribution as a function of −log[H] is shown in Figure 4 for different metal-to-ligand ratios. Published cadmium−malate complexation constants are presented in Table 4. Regarding the quality of the available data, the same types of considerations discussed above for the cadmium−succinate system apply in this case.

D. Error Treatment. Changes in ionic strength that occur during the titrations under the experimental conditions used in the present work are shown in Tables 5 and 6. Data for only one protonation and one metal complexation curve are shown. Similar variations were obtained in all protonation and complexation titrations. Constants corrected for ionic strength variations are given in Table 2 (DHC option values). Introducing a correction for changes in ionic strength has only a minor influence on the calculated constant values. This is to be expected, since the experimental conditions were chosen so as to minimize such changes. Note, however, that the ionic strength is always higher than the theoretical value. Thus, ionic strength correction ensures that all constants refer precisely to the specified reference ionic strength.

The effect of changes in liquid junction potential and selectivity of the electrodes was assessed. Unfortunately, the parameters required for such calculations can only be approximated from literature values, which are scanty and of doubtful applicability. Therefore, estimations obtained should only be considered at a qualitative level.

As expected, the effect of sodium ion interference over the pH range used in the titrations is not significant, even at the sodium concentrations present in this study.

Tables 5 and 6 also show the liquid-junction potentials calculated from the Henderson equation for a saturated potassium chloride bridge. Although these types of bridges are not as well characterized as constant ionic strength

Table 3. Literature Cadmium Succinate Stability Constants in Aqueous Solution[a]

suggested species formed	complexation constants[b]	T/°C	I/mol·dm^{-3}	technique	ref
ML	2.2	20	0.05 ?	Cd ISE	Ferrell et al., 1934[c]
ML	2.1	25	0.10 $NaClO_4$	potentiometry	Yasuda et al., 1960
$M + L \rightleftharpoons ML$	1.67	20	1.0 $NaClO_4$	potentiometry	Schwarzenbach and Szilard, 1962
$ML + L \rightleftharpoons ML_2$	1.12				
$M + HL \rightleftharpoons MLH$	0.99				
ML	1.65	30	2.0 NaClO4	polarography	Gaur and Palrecha, 1968
ML_2	2.76			pH = 7	
ML_3	3.05				
ML	1.47	27	2.1 KNO_3	polarography	Khurana and Gupta, 1972
ML_2	2.292			pH = 7.0	
ML_3	2.740				
ML	1.60	25	?	EMF	Gu, 1976[d]
ML_2	2.32				
ML	2.81	25	0.1 KNO_3	polarography	Bolotov et al., 1976
ML_2	3.62		20% v/v EtOH		
ML_3	4.14				
ML	1.54 ± 0.06	25	3.0 $NaNO_3$	polarography	Jadhav et al., 1978a
ML_2	2.00 ± 0.04				
ML_3	3.08 ± 0.01				
ML	1.65	25	3.0 KNO_3	polarography	Jadhav et al., 1978b
ML_2	2.18 ± 0.06			pH = 6.6	
ML_3	3.32 ± 0.08				
ML	1.653	20	2.0 KNO_3	polarography	Sharma and Gaur, 1978
ML_2	2.763				
ML_3	3.045				
ML	1.580	30			
ML_2	2.699				
ML_3	2.977				
ML	1.653	25	2.0 KNO_3	polarography	Sharma et al., 1980
ML_2	2.763				
ML_3	3.045				
ML	1.597	35			
ML_2	2.699				
ML_3	2.981				
ML	2.51	25	0.1 KNO_3	polarography	Kharitonov et al., 1980
ML_2	4.02		20% v/v EtOH		
ML	1.30	25	2.0 $NaNO_3$	polarography	Shivhare and Singh, 1981
ML_2	2.0				
ML_3	3.0				
ML	2.301	25	1.0 KNO_3	polarography	Garg et al., 1983a,b
ML_2	3.097				
ML_3	3.699				
ML	1.78	25	3 $LiClO_4$	potentiometry	Matsui, 1984
ML_2	3.08				
ML	2.30	25	1.5 KNO_3	polarography	Garg et al., 1984
ML_2	3.10				
ML_3	3.70				
ML	1.48	30	1.5 KNO_3	polarography	Kumari et al., 1985
ML_2	2.90		50% v/v		
ML_3	3.40		dioxane		
ML	1.56	25	1 $NaNO_3$	DPP	Killa and Zaky, 1985
ML_2	2.47				
ML_3	2.86				
ML	1.47 ± 0.07	25	1.5 KNO_3	polarography	Dhuley and Bidkar, 1987
ML_2	2.30 ± 0.04			pH = 7	
ML_3	3.14 ± 0.06				
ML	1.7	25	1.0 $NaClO_4$	polarography	Rodriguez-Placeres et al., 1988
ML_2	2.7			pH = 7	
ML_3	3.4				
ML	0.66	25	1.0 $NaClO_4$	polarography	Rodriguez Placeres et al., 1990
ML_2	2.65			pH = 7	
ML_3	3.34				
ML	1.90	30	0.1 KNO_3	polarography	Sindhu et al., 1991
ML_2	3.28			pH = 9.5	
ML	2.27	25	1.0 $NaClO_4$	polarography	Jain et al., 1992
ML_2	3.10			pH = 8	
ML_3	3.65				
ML	2.60	30	0.1 KNO_3	polarography	Sindhu et al., 1994
ML_2	4.30			pH = 9.5	
ML	2.03	25	0.1 KNO_3	potentiometry	Vasil'ev et al., 1997

[a] More data can probably be found in Guru and Mahajani, 1975; Kharitonov and Kharitonova, 1982; Katib and Killa, 1992; Kang et al., 1993; Zhang et al., 1993. [b] Constants are β values unless an explicit reaction is given. [c] Values as quoted in Sillén (1964) and in the SC-Database (Pettit and Powell, 1997). These values are inconsistent with the original source. [d] As quoted in the SC-Database (Pettit and Powell, 1997). Original publication was unobtainable.

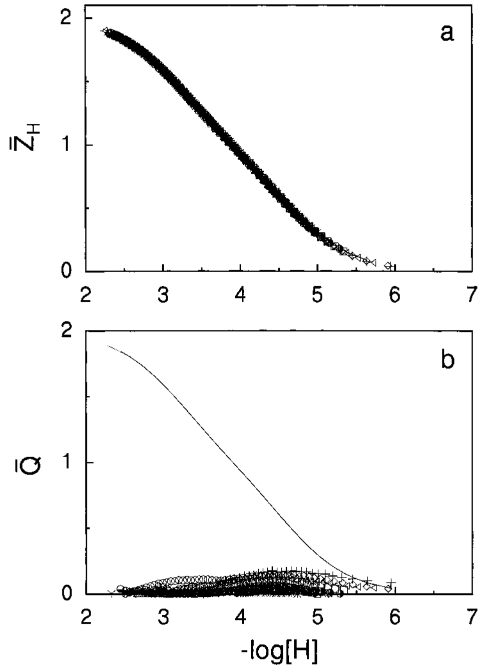

Figure 3. Experimental protonation (a) and deprotonation (b) curves for the Cd^{2+}-mal-H^+ system. Different symbols refer to different titrations. The theoretical protonation curve for the ligand in the absence of metal is shown as a solid line.

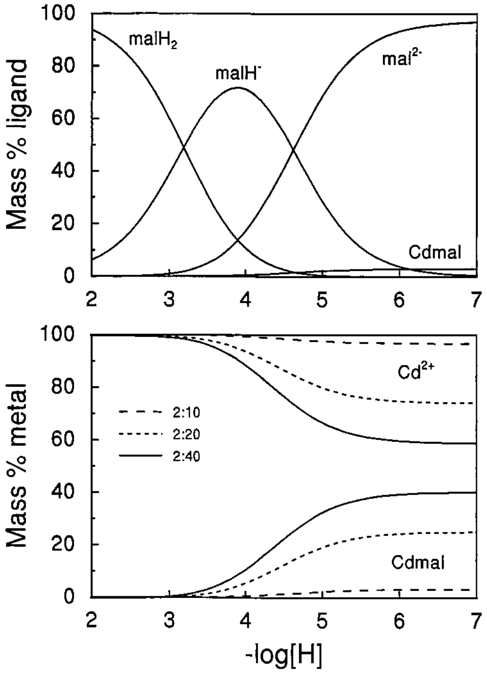

Figure 4. Ligand and metal species distribution as a function of −log[H] for different Cd(II) and malate ratios. M/L concentrations (in mmol·dm^{-3}) are indicated in the figures.

ones, they are commonly employed because they are easier to use while reducing the size of the junction potential. Values in Tables 5 and 6 show that errors arising from junction potentials are constant and relatively small under our working conditions. Ionic conductance values used in the calculations are given at the bottom of Tables 5 and 6. Although the effect of variation in the liquid-junction potential may affect significantly any stability constant determination, rigorous correction for this effect was not attempted here because it would require better estimations of the ionic conductances of all the species involved than those currently available.

As mentioned above, the reliability of most of the previously published stability constants for cadmium succinate and cadmium malate systems looks very poor. However, it is very difficult to judge the likely reliability of any set of published constants and even of your own determined constants. Two different aspects need to be considered, precision and accuracy of the calculated constants.

Conventional standard deviations of formation constants as calculated by the currently used programs significantly underestimate the spread of results likely to be obtained if the measurements were repeated independently many times (Braibanti et al., 1982, 1987). It has been proposed that analysis of titration data by applying a Monte Carlo technique would allow a better estimation of the precision of formation constants (May and Murray, 1988b). The Monte Carlo method is a means of simulating the measurements which might be made on a system if the whole experiments were to be repeated by a large number of independent investigators. As expected, the standard deviations obtained by applying this technique (program ESTA3B, modified to incorporate a better random number generator (Press et al., 1992)) are poorer than those obtained conventionally because they better reflect the true effect of random errors on the formation constant values.

As far as accuracy is concerned, the relatively small effect on the calculated values of the systematic errors considered above highlights the fact that most of the discrepancies between published stability constant values probably stem from other sources of errors, such as low degree of independence between titrations, errors in total concentrations, temperature control, and so forth, as well as from calculation procedures. The effect of systematic errors unavoidably present in titration parameters can be minimized through their simultaneous optimization with the constants. However, simultaneous optimization of all titration parameters is not possible due to correlation-derived effects, and the danger of false optimization should always be considered. The Monte Carlo method may help to improve the accuracy of the calculated constant via the search for the best set of parameters to refine. The procedure consists of testing all possible parameter combinations on sets of data simulated by imposing random errors as described above. (See May and Murray, 1988b for a detailed discussion of the method.) Values obtained by application of a Monte Carlo procedure, including simultaneous optimization of constants and the best set of titration parameters to our data, are quoted in Table 2 as “best results”. The closeness of the results obtained with and without simultaneous refinement of titration parameters suggests that no important systematic errors were present in the experimental data used. They support the accuracy of our calculated values.

Voltammetric Studies. A. Cyclic Voltammetry. On addition of malic acid (9.85−69.4 mmol·dm^{-3}) to Cd(II) (0.2 mmol·dm^{-3}) there was no shift in the Cd(II) peaks. However, a second (irreversible) cathodic peak at approximately −0.84 V (versus the Ag/AgC/Cl^- (sat.) electrode) was observed, the height of which increased as the concentration of malic acid was increased (Figure 5a). This peak corresponded to reduction of free malic acid, as verified by separate measurements on a ligand-only solution (data not shown).

Small shifts in the potential of the cathodic and anodic Cd(II) peaks (toward more negative potentials) and a

Table 4. Literature Cadmium Malate Stability Constants in Aqueous Solution[a]

suggested species formed	complexation constants[b]	T/°C	I/mol·dm^{-3}	technique	ref
$M + H_2L \rightleftharpoons MLH_2$	1.34	20	0.1 $NaClO_4$	potentiometry	Campi, 1963
$M + HL \rightleftharpoons MLH$	2.36				
ML	1.40	25	2.0 ?	polarography	Topuzovski, 1972[c]
ML_2	3.00				
ML_3	3.28				
ML	1.9	27	0.1 KNO_3	polarography	Khurana and Gupta, 1973
ML_2	2.8				
ML_3	3.4				
$M + H_2L \rightleftharpoons MLH_2$	0.57				
ML	1.845	27	2.1 KNO_3	polarography	Khurana et al., 1973
ML_2	2.778			pH = 7	
ML_3	3.362				
ML	2.41	25	0.1 KNO_3	polarography	Bolotov et al., 1976
ML_2	2.92		20% v/v EtOH		
ML_3	4.03				
ML	1.54 ± 0.15	25	2.1 $NaNO_3$	polarography	Jadhav and Bhobe, 1977
ML_2	2.60 ± 0.05			pH = 6.5−6.7	
ML_3	3.42 ± 0.05				
ML	2.36	25	0.1 KNO_3		Kharitonov et al., 1980
ML_2	4.00		20% v/v EtOH		
ML	1.90	30	1.5 KNO_3	polarography	Sachan et al., 1982
ML_2	2.80				
ML_3	3.40				
ML	1.90	30	1.0 KNO_3	polarography	Gupta et al., 1983
ML_2	2.80				
ML_3	3.40				
ML	1.90	30	1.5 KNO_3	polarography	Kumari et al., 1985
ML_2	2.80		50% v/v dioxane		
ML_3	3.46				

[a] More data can probably be found in Kharitonov and Kharitonova, 1982. [b] Constants are β values unless an explicit reaction is given. [c] Values as quoted in Perrin (1979) and in the SC-Database (Pettit and Powell, 1997). Original publication was unobtainable.

Table 5. Simulated Ionic Strength Changes, Liquid-Junction Potentials, and Sodium Ion Interference for a Titration of the Suc-H$^+$ System[a]

		mass % of Cd^{2+} in species				
volume added/cm^{-3}	−log[H]	suc^{2-}	suc-H$^+$	suc-H_2	I/mol·dm^{-3}	E^{LJ} [b]/mV
0.00	2.28	0	2	98	0.150	0.79
0.36	2.42	0	3	97	0.150	0.80
0.72	2.60	0	4	96	0.149	0.81
1.08	2.82	0	7	93	0.149	0.82
1.44	3.08	0	12	88	0.149	0.81
1.80	3.32	0	19	81	0.149	0.80
2.16	3.51	0	27	73	0.150	0.78
2.52	3.68	0	36	64	0.151	0.76
2.88	3.83	2	42	56	0.151	0.74
3.24	3.96	3	49	48	0.152	0.72
3.60	4.10	5	56	41	0.153	0.70
3.96	4.22	7	61	32	0.154	0.69
4.32	4.35	10	65	25	0.155	0.67
4.68	4.48	13	67	20	0.156	0.65
5.04	4.61	18	67	15	0.157	0.63
5.40	4.74	24	66	10	0.158	0.62
5.76	4.86	30	62	8	0.159	0.60
6.12	4.99	37	58	5	0.160	0.59
6.48	5.15	45	52	3	0.162	0.57
6.84	5.26	54	44	2	0.163	0.56
7.20	5.41	62	36	1	0.165	0.55
7.56	5.59	71	28	1	0.166	0.53
7.92	5.81	81	19	0	0.168	0.52
8.28	6.16	90	10	0	0.169	0.51

[a] Data shown correspond to succinate protonation titration 5 in Table 1. Only one in every two points is shown. [b] Ionic conductance values used. Bridge: K^+, 36.0; Cl^-, −39.0. Solution: K^+, 81.0; Na^+, 53.0; Cl^-, −83.0; H^+, 125.0; OH^-, −100.0. suc, −10 (Parsons, 1959; May et al., 1985).

Table 6. Simulated Ionic Strength Changes, Liquid-Junction Potentials, and Sodium Ion Interference for a Titration of the Cd^{2+}-suc-H$^+$ System[a]

		mass % of Cd^{2+} in species			
volume added/cm^3	−log[H]	Cd-suc-H$^+$	Cd-suc	I/mol·dm^{-3}	E^{LJ} [b]/mV
0.00	2.61	0	1	0.152	0.85
0.40	2.82	0	1	0.152	0.85
0.80	3.04	0	2	0.152	0.85
1.20	3.24	0	3	0.153	0.83
1.60	3.42	0	4	0.153	0.82
2.00	3.56	0	5	0.153	0.80
2.40	3.69	1	6	0.154	0.78
2.80	3.81	1	7	0.154	0.76
3.20	3.92	1	8	0.155	0.75
3.60	4.02	2	8	0.156	0.73
4.00	4.12	3	9	0.156	0.71
4.40	4.22	4	9	0.157	0.69
4.80	4.32	5	9	0.158	0.68
5.20	4.42	6	10	0.159	0.66
5.60	4.52	7	9	0.160	0.64
6.00	4.62	9	9	0.160	0.63
6.40	4.72	11	9	0.162	0.61
6.80	4.82	13	8	0.162	0.60
7.20	4.93	15	7	0.164	0.59
7.60	5.03	17	7	0.165	0.57
8.00	5.14	19	6	0.166	0.56
8.40	5.24	21	5	0.167	0.55
8.80	5.36	23	4	0.168	0.54
9.20	5.49	25	3	0.169	0.52
9.60	5.64	27	3	0.171	0.51
10.00	5.83	29	2	0.172	0.50

[a] Data shown correspond to complexation titration 2 in Table 1. Only one in every two points is shown. [b] Ionic conductance values used. Bridge: K^+, 36.0; Cl^-, −39.0. Solution: K^+, 81.0; Na^+, 53.0; Cl^-, −83.0; H^+, 125.0; OH^-, −100.0. suc, −10; Cd^{2+}, 47.3 (Parsons, 1959; May et al., 1985).

reduction in the peak currents were observed on addition of succinic acid (9.85−69.4 mmol·dm^{-3}) to Cd(II) solution (0.2 mmol·dm^{-3}) (Figure 5b). No additional peaks corresponding to ligand-based processes were observed.

B. Differential Pulse Polarography. Measurements on a Cd(II)-only containing solution showed reversible behavior; $w_{1/2} = 66$ mV, $E_p = -0.556$ V.

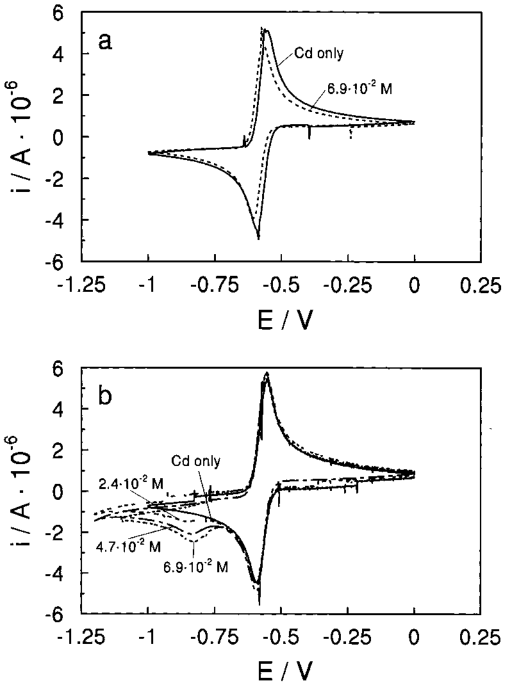

Figure 5. Cyclic voltammograms, at pH 8.2, 150 mmol·dm^{-3} $NaClO_4$, and [Cd(II)] = 0.2 mmol·dm^{-3} for (a) the Cd(II)−succinic acid system and (b) the Cd(II)−malic acid system. Ligand concentrations are indicated in the figures.

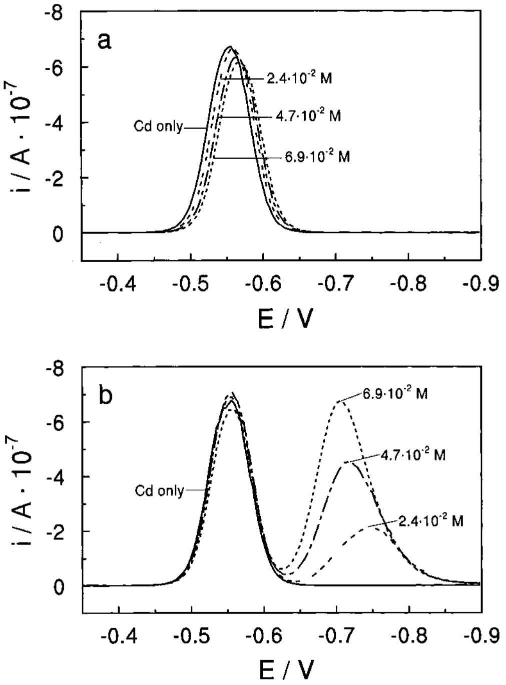

Figure 6. Differential pulse polarograms at pH 8.2, 150 mmol·dm^{-3} $NaClO_4$, and [Cd(II)] = 0.2 mmol·dm^{-3} for (a) the Cd(II)−succinic acid system and (b) the Cd(II)-malic acid system. Ligand concentrations are indicated in the figures.

In the presence of malic acid, the DPP cathodic scan showed a peak at −0.556 V corresponding to reduction of Cd(II), the magnitude and position of which did not change as the concentration of malic acid was increased. A second peak was observed at approximately −0.71 V, corresponding to reduction of the free ligand (Figure 6a).

In the presence of increasing concentrations of succinic acid the DPP cathodic peak current for Cd(II) decreased, and the peak potential shifted to more negative potentials (by 12 mV in the presence of 69.4 mmol·dm^{-3} succinic acid) (Figure 6b).

The negligible (malic acid) or very small (succinic acid) peak potential shifts observed in the presence of these ligands preclude the reliable determination of stability constants from the electrochemical data. The results are consistent with formation of very weak, labile complexes. For the Cd(II)−succinic acid system, a peak potential shift of 12 mV corresponds to a log K_1 value of 1.41, which is close to the value determined potentiometrically. Although the Borax buffer medium is itself weakly complexing for Cd (log $K_1 = 1.42$, log $K_2 = 1.28$ (in 0.7 mol dm^{-3} KNO_3, 25 °C); Pettit and Powell, 1997), the fact that the voltammetrically determined log K_1 value is comparable to the potentiometric one indicates that it did not interfere with our potential shift measurements. It was verified that, for the more complexing Cd(II)−alanine system (Gonçalves and Dos Santos, 1984), results consistent with reported stability constants were obtained.

The DPP results for the Cd(II)−succinic acid system (Figure 6b), viz a decrease in peak height and a shift in peak potential to more negative potentials, may imply that the polarographic limiting current has a kinetic character (Gonçalves and Dos Santos, 1984). The slight reduction in CV peak currents in the presence of succinic acid is also consistent with this proposal (Figure 5b).

The very small shifts in the electrochemical signals in the presence of the ligands are consistent with the low values for the stability constants determined by potentiometry. Many of the stability constants reported for the Cd(II) malate and succinate systems have been determined polarographically (Tables 3 and 4). However, in most of the existing publications, very high ligand concentrations were used, which would have made a significant contribution to, and in some cases even exceeded, the stated ionic strength (inert electrolyte concentration) (e.g. Khurana and Gupta 1972, 1973). Under such conditions the measured potentials may be distorted, and hence erroneous interpretations could be made (Dandoy and Gierst, 1961; Verdier and Rouelle, 1965; Urbañska, 1992).

A polarographic study on the Ni succinate system (Urbañska, 1992), under conditions comparable to those used in the present work ([Ni] = 0.1 mmol·dm^{-3}, [L] = 8 mmol·dm^{-3}) gave results consistent with our observations, that is, an $E_{1/2}$ shift of approximately 10 mV and a decrease in the limiting current as [L] increased. For this system, NiL was found to be the only species formed (log $K_1 = 1.84$).

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