

联合处理电位法和极谱法得到的实验数据确定金属配合物稳定常数

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Determination of Metal Complex Stability Constants by a Unified Treatment Method for Potentiometric and Polarographic Data

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The cadmium(II)-glycinamide system was modeled and its stability constants were calculated by a unified mathematical treatment for experimental data obtained from ion selective electrode (ISE) and differential pulse polarography (DPP). It has been shown that very much the same experimental complex formation curve (ECFC) and theoretical complex formation curve (TCFC) could be given from both experimental techniques for the same experimental conditions, such as the same total ligand $c(L_T)$ and metal ion $c(M_T)$ concentrations. The combination of the two techniques is of many advantages as ISE can be performed at low a $c(L_T):c(M_T)$ ratio and significantly higher $c(M_T)$, whereas DPP could be used well at larger the $c(L_T):c(M_T)$ ratio and very low $c(M_T)$. This makes it possible to study a metal-ligand system in much broader range of experimental conditions that, in turn, provides us more data and information about the metal-ligand system of interest. Application of the unified mathematical treatment to the cadmium-glycinamide system in this paper, three new complexes MHL, ML_3 and $ML_3(OH)$ as well as two complexes ML and ML_2 , reported in literatures, could be modeled and all their stability constants have been refined.

Keywords: metal complex polarography potentiometry stability constant

0 Introduction

The experimental methods applied in the field of determination of metal complex stability constants should be classified into two ways—one is an equilibrium technique and another is a dynamic technique^[1]. The equilibrium technique, such as glass electrode po-

tentiometry (GEP), ion sensitive or ion selective electrodes (ISE), means that the concentrations of all species present in a sample are the same in bulk as well as at the surface of a sensor during the experimental process. ISE are frequently used in the field of a metal-ligand equilibrium study^[2-5] and with recent improvements and extension of the linear response of

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ISE^[6,7] they seem to be an attractive option in the determination of metal complex stability constants. Polarography, or more generally voltammetry, is a dynamic technique as opposed to GEP or ISE that can be thought as a static electrochemical technique. The electron transfer process occurring at the electrode/solution interface causes significant changes in the concentration of metal species in the vicinity of the working electrode when polarography/voltammetry is performed. The composition of ligand species can be regarded as unaffected by the electron transfer provided that there is a significant excess of the ligand present in a solution. Any rigorous theory describing processes occurring at the electrode/solution interface would have to include thermodynamic, kinetic and transport phenomena, at least. Not surprisingly, there is not a general theory to date that would allow one to study by voltammetry any kind of metal complexes, such as fully labile, nonlabile and inert metal-ligand systems^[8,9]. However, it has been shown recently that it is possible to evaluate stability constants of many metal complex systems^[10-13] from the analysis of the labile part of the metal-ligand system when polarography was employed at a fixed total ligand to metal concentration ratio and various pH values.

The aim of this work is to demonstrate, in principle, that the same mathematical model and refinement procedures, which were written^[14] on a concept of experimental and theoretical complex formation curves (ECFC and TCFC) used previously in a study of metal complexes by a dynamic technique (polarography or voltammetry), could be directly used for evaluation of experimental data coming from the static technique (ISE). A metal-ligand system, cadmium-glycinamide, was chosen to verify the validity of the proposed procedure. Cadmium complexes with the ligand glycinamide can be classified as fully labile and their reduction can be regarded as reversible on the DPP time-scale.

1 Experimental

1.1 Materials and Instruments

The ligand, glycinamide, was obtained from Aldrich, and all other reagents used were of analytical grade. The $1.00 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ stock solution of cadmi-

um nitrate for the calibration of ISE was prepared in $0.01 \text{ mol} \cdot \text{L}^{-1}$ nitric acid.

All experiments were performed in a jacketed glass vessel, equipped with a magnetic stirrer, and thermostatic control at 298 K by water circulating from a constant temperature bath. The pH of solutions and potential of ISE were measured to $\pm 0.1 \text{ mV} (\pm 0.001 \text{ pH unit})$ with PHI 72 meters (Beckman). A combination glass electrode and a solid-state membrane cadmium ion selective electrode (both Metrohm) were used. Differential pulse polarograms were obtained with a Metrohm Model 663 VA stand. A multi-mode electrode was employed as the working electrode and used in the dropping mercury electrode mode with a dropping time of 2 s. A silver/silver chloride electrode and a platinum electrode were used as reference and auxiliary electrodes, respectively. A pulse height of 50 mV and step height of 4 mV were used. The pulse width and integration time were set to 200 ms and 90ms, respectively. High purity nitrogen was used for deaeration of the sample solutions.

1.2 Polarography

In a typical run, the first polarogram was recorded for a solution containing about $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ of Cd(II) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaNO_3 adjusted to a pH of about 4, as formation of the complexes ML_n was expected to start at slightly higher pH values. Several different total-ligand to total-metal concentration ratios were used and were prepared by an addition of the appropriate amount of the solid ligand glycinamide to the vessel containing a cadmium ion solution. After recording a polarogram, the pH of the solution was increased in steps of about 0.100~0.150 pH units, by addition of a standard NaOH solution from a microburette graduated to 0.01 mL, and after each addition a new polarogram was recorded. In this way a set of 40~50 polarograms were obtained for each $c(\text{L}_T):c(\text{M}_T)$ ratio as a function of pH. Polarograms of the ligand alone as a function of pH were also run in a similar way. It has been checked that equilibration of the metal-ligand solution would be completed within a few minutes. All polarograms were recorded on solutions with an ionic strength of $0.1 \text{ mol} \cdot \text{L}^{-1}$.

1.3 ISE

The experiments of ISE were done as the same

procedure as polarography. The cadmium ISE was stored in a $0.1 \text{ mol} \cdot \text{L}^{-1}$ cadmium ion solution. Prior the experiment, the working electrode surface was refreshed by polishing with a paste, followed by thorough rinsing with water and conditioning of the electrode in $0.1 \text{ mol} \cdot \text{L}^{-1}$ Cd^{2+} solution for at least 1 hour. Two calibration procedures were tested before and after an experiment of metal complexes. Either standard solutions were prepared in a broad total cadmium concentration range (between 0.1 and $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) or in one order of magnitude concentration range with $c(\text{M}_\text{T})$ (a total cadmium concentration used in the study of metal complexes) being in the middle.

2 Data Treatment

When a set of differential pulse polarograms, recorded on a single solution sample and obtained at a fixed $c(\text{L}_\text{T}):c(\text{M}_\text{T})$ as a function of pH, shows a single and well shaped DPP peak, then a metal-ligand system is classified as fully labile^[8,9] on the differential pulse polarographic time scale and its electrochemical reduction on mercury electrode could be considered as thermodynamically reversible processes. The single DPP peak then represents all metal species present in the solution sample at a particular pH value. This peak usually shifts towards more negative potential and vary in height when consecutive metal complexes are formed. For thermodynamically reversible processes, the shift in the peak potential and the variation in the peak height (the latter one is caused mainly by the change in a diffusion coefficient) is described mathematically in terms of changes in the composition of the solution, when the experiment is performed at fixed $c(\text{M}_\text{T}):c(\text{L}_\text{T})$ ratio and varying pH, by the following equation^[11,12]

$$\begin{aligned} (E_\text{p}(\text{M}) - E_\text{p}(\text{comp}))_{\text{pH}} - \frac{RT}{nF} \ln \left(\frac{I_\text{p}(\text{comp})}{I_\text{p}(\text{M})} \right)_{\text{pH}} \\ = \frac{RT}{nF} \ln \left(\frac{c(\text{M}_\text{T})}{c(\text{M})} \right)_{\text{pH}} \end{aligned} \quad (1)$$

where $E_\text{p}(\text{M})$ and $E_\text{p}(\text{comp})$ stand for the peak potential in the absence and the presence of metal complexes, respectively, $I_\text{p}(\text{M})$ and $I_\text{p}(\text{comp})$ stand for the peak current in the absence and the presence of metal complexes, respectively, $c(\text{M}_\text{T})$ and $c(\text{M})$ stand for the

(free) metal ion concentration in the absence and the presence of metal complexes, respectively. The (free) metal ion concentration is equal to the total metal ion concentration in the absence of metal complexes.

When the experiments of ISE were done, the change or shift in the potential of ISE for the formation of metal complexes could be expressed as

$$(E(\text{M}) - E(\text{comp}))_{\text{pH}} = \text{SLOPE} \ln \left(\frac{c(\text{M}_\text{T})}{c(\text{M})} \right)_{\text{pH}} \quad (2)$$

where $E(\text{M})$ and $E(\text{comp})$ indicate the potential of ISE obtained in the absence and the presence of metal complexes, respectively. The value of SLOPE is obtained, prior and after an experiment of metal complexes, from the calibration procedures performed on standard metal ion solutions.

The left-hand sides of equations **1** and **2** contain experimental terms available from the polarographic technique and the ISE technique, respectively. Since the formation of metal complexes is pH dependent, the values of the left-hand sides of equations **1** and **2** will change with pH increase of the solution sample. Graphs of values of the left-hand sides of equations **1** and **2** vs pH are usually called experimental complex formation curves (ECFC). The ECFC will be characteristic for a particular metal-ligand system as a function of all metal species formed in the solution at a particular $c(\text{M}_\text{T}):c(\text{L}_\text{T})$ ratio.

The right-hand sides of equations **1** and **2** contain the total and free metal ion concentration. The total metal concentration in a solution sample is known but the free metal ion concentration is not available from the DPP or ISE experiment. The free metal ion concentration could be calculated from mass-balance equations written for the assumed model for both techniques employed here. Graphs of values of the right-hand sides of equations **1** and **2** vs pH are usually called theoretical complex formation curves (TCFC). The stability constants (included in the mass-balance equations) for metal complexes formed are varied and refined to obtained the best fit of the TCFC into the ECFC.

The mass-balance equations are written for the assumed metal-ligand model that should include the complexes for calculated stability constants, $\text{M}_\text{x}\text{L}_\text{y}\text{H}_\text{z}$, $\text{M}_\text{x}\text{L}_\text{y}$, and $\text{M}_\text{x}\text{L}_\text{y}(\text{OH})_\text{z}$, and the complexes for known

stability constants, $M_x(OH)_y$ and H_xL_y .

$$c(M_T)=c(M) + \sum \sum xc(M_x(OH)_y) + \sum \sum \sum xc(M_xL_yH_z) + \sum \sum xc(M_xL_y) + \sum \sum \sum xc(M_xL_y(OH)_z) \quad (3)$$

$$c(L_T)=c(L) + \sum \sum yc(H_xL_y) + \sum \sum \sum yc(M_xL_yH_z) + \sum \sum yc(M_xL_y) + \sum \sum \sum yc(M_xL_y(OH)_z) \quad (4)$$

For the cadmium-glycinamide system proposed in this work, Equation 3 and 4 would become

$$c(M_T)=c(M) + \beta_{MHL}c(M)c(H)c(L) + \beta_{ML}c(M)c(L) + \beta_{ML_2}c(M)c(L)^2 + \beta_{ML_3}c(M)c(L)^3 + \beta_{ML_3(OH)}c(M)c(L)^3c(OH) + \beta_{M(OH)}c(M)c(OH) + \beta_{M(OH)_2}c(M)c(OH)^2 + \beta_{M(OH)_3}c(M)c(OH)^3 + \beta_{M(OH)_4}c(M)c(OH)^4 + 2\beta_{M_2(OH)}c(M)^2c(OH) + 4\beta_{M_3(OH)}c(M)^4c(OH)^4 \quad (5)$$

$$c(L_T)=c(L) + \beta_{HL}c(H)c(L) + \beta_{H_2L}c(H)^2c(L) + \beta_{MHL}c(M)c(H)c(L) + \beta_{ML}c(M)c(L) + 2\beta_{ML_2}c(M)c(L)^2 + 3\beta_{ML_3}c(M)c(L)^3 + 3\beta_{ML_3(OH)}c(M)c(L)^3c(OH) \quad (6)$$

The stability constants of metal complexes that would be refined by fitting the TCFC into the ECFC are marked as bold. The mass-balance eqs. 5 and 6 are solved by the computer program CFC- II specially written for treatment of the experimental data obtained from metal-ligand systems. The protonation constants of the ligand^[15], dissociation constant of water^[15] and

Table 1 Overall Stability Constants for Cd(II) Complexes with OH⁻, Protonation Constants for the Ligand Glycinamide(L) and Dissociation Constant of Water (all from^[15]) Included in the Cd-L-OH Model and Used in the Refinement Procedure for DPP and ISE Data. All lgβ Values are Reported at 298 K and an Ionic Strength of 0.1mol·L⁻¹.

equilibrium	lgβ
$Cd^{2+} + OH^- = Cd(OH)^+$	4.0
$Cd^{2+} + 2OH^- = Cd(OH)_2$	7.7
$Cd^{2+} + 3OH^- = Cd(OH)_3^-$	10.3
$Cd^{2+} + 4OH^- = Cd(OH)_4^{2-}$	12.0
$2Cd^{2+} + OH^- = Cd_2(OH)^+$	5.06
$4Cd^{2+} + 4OH^- = Cd_4(OH)_4^{4+}$	24.9
$H^+ + L^- = HL$	7.98
$H^+ + OH^- = H_2O$	13.78

hydrolysis constants for cadmium^[15] (Table 1) were kept fixed during the refinement operations. At any point of experiment the total concentrations of the ligand and the metal ion, as well as pH, are known. Equations 5 and 6 are solved simultaneously and the computed value of the free metal ion concentration is used by equations 1 and 2 to generate the theoretical complex formation curves, TCFC, for polarographic and ISE techniques. The refined stability constants are varied till the best fit of the TCFC into the ECFC is given.

3 Results and Discussion

3.1 Polarographic Study

A set of differential pulse polarograms, recorded in the Cd(II)-glycinamide system as a function of pH, shows a single and well shaped DPP wave which peak width is about 62 mV. The variation in DPP peak height vs pH for the Cd-glycinamide system is shown in Fig.1, in which curves a, b and c stand for the recorded peak height (I_p (comp)), the expected peak height ($I_p(M)$) if the metal complexes were not formed (the observed decrease at high pH is caused by dilution of a sample) and the normalized peak height ($I_p(comp) / I_p(M)$), respectively. There is almost no change in normalized peak height vs pH for the Cd-glycinamide system, so it could be thought that all complexes formed in the solution sample are labile and the electrochemical reduction process occurring at mercury electrode could be regarded as reversible.

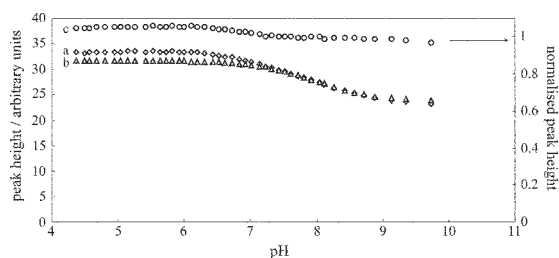


Fig.1 Variation in the DPP peak current with pH for the Cd-glycinamide complex system at 25 °C and an ionic strength of 0.1 mol·L⁻¹ (NaNO₃). All polarograms were recorded on one solution sample containing initially $c(M_T)=3.75 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $c(L_T):c(M_T)=100$. Curves a, b and c are described in the article

Two relationships, observed shift in DPP peak potential plotted vs $\lg c(L)$ and observed shift in DPP peak potential plotted vs pH, are usually used for the prediction of species formed and will be discussed here briefly. The variation in DPP peak potential E_p as a function of the free ligand concentration is given in Fig.2. The continuous change in the slope is observed with the solid line indicating the maximum value of about 90 mV per lg unit. It has been well known that when complexes ML , ML_2 and ML_3 are reduced at the electrode, the slopes for the observed shift in DPP peak potential plotted vs $\lg c(L)$ should be 30 mV/ $\lg c(L)$, 60 mV/ $\lg c(L)$ and 90 mV/ $\lg c(L)$, respectively. There is not a significant shift in the peak potential up to pH of about 6 (Fig.3). This might indicate the absence of cadmium complexes with glycineamide. However, one cannot exclude the possibility of the formation of $M(HL)$ as it would not cause the shift in the peak potential. This is because the formation of $M(HL)$ would occur in the pH region where HL is the major form of the ligand and the reduction of $M(HL)$ would not involve protons. Above pH 9 the free ligand L predominates in a solution and one would not

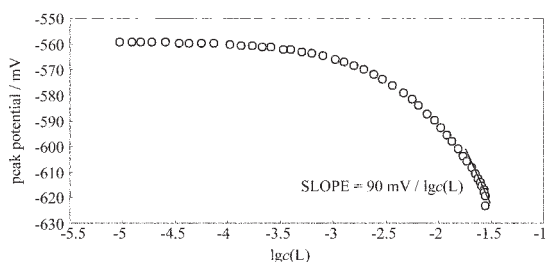


Fig.2 Variation in DPP peak potential E_p for the Cd-glycineamide system as a function of the free ligand concentration (experimental parameters as in Fig.1)

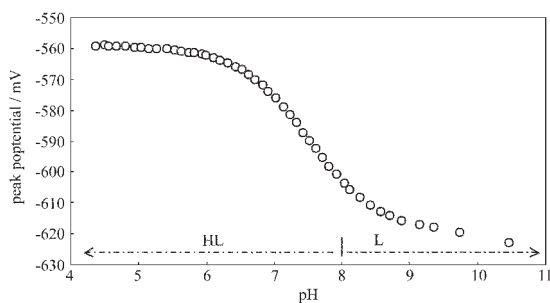


Fig.3 Variation in DPP peak potential E_p for the Cd-glycineamide system as a function of pH (experimental parameters as in Fig.1)

expect the shift in the peak potential when only ML_3 is present in the solution. Instead, There is a shift in DPP peak potential above pH 9 (Fig.3) that indicates the formation of a metal complex containing OH group, $ML_3(OH)$.

From the above analysis of the shift in the peak potential vs $\lg c(L)$ and pH, it can be predicted that five cadmium complexes, MHL , ML , ML_2 , ML_3 and $ML_3(OH)$, might be present in the cadmium-glycineamide system. The computer analysis procedure CFC-II would verify whether this model is right and evaluate their stability constants. The experimental corrected shift in the peak potential was calculated for each datum from the left-hand side of equation 1 and plotted vs pH to give the experimental complex formation curve (ECFC) for the Cd-glycineamide system studied. As an example, the ECFCs obtained at $c(L_T):c(M_T)$ ratios of about 100 and 50 are seen in Fig.4 (circles). The theoretical complex formation curves (TCFCs) for the above model are also seen in Fig.4 (lines). One can see that the fit of TCFC into ECFC for the proposed model is very excellent, and the refined values for the stability constants are shown in Table 2. If the complexes MHL and $ML_3(OH)$ are excluded from the model, the overall fit as well as standard deviations in stability constants for metal complexes were significantly larger than the full metal-ligand model.

3.2 ISE Study

The commercial ISE employed comes with a manufacturer specification that indicates the possibility of its use in a broad pH range (between 2 and 10) and a linear response down to about $1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ of Cd(II). Since the experiments were performed at the total metal ion concentration between 1×10^{-3} and $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, the electrode response was tested only down to $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of Cd(II) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaNO_3 . The obtained calibration plots were linear with a slightly different slope from experiment to experiment. The slope of the ISE, used for initial refinement operations, was evaluated prior and after the experiment. It has been established that the electrode potential was stable in time (several hours) to $\pm 0.4 \text{ mV}$. Similar stability in the electrode response was ob-

Table 2 Overall Stability Constants for Ca(II) with Glycinamide Refined in this Work by DPP and ISE (Using the Same Curve Fitting Procedure as Described in the Text) at 298 K and $\mu=0.1 \text{ mol} \cdot \text{L}^{-1}$

exp	ratio	$c(\text{M}_\text{T})$ / ($\text{mol} \cdot \text{L}^{-1}$)	$\lg\beta$					fit / ($\pm\text{mV}$)	ref.
			MHL	ML	ML_2	ML_3	$\text{ML}_3(\text{OH})$		
DPP	100	3.75×10^{-4}	9.38 ± 0.03	2.89 ± 0.04	4.86 ± 0.13	6.82 ± 0.03	10.24 ± 0.14	0.04	this work
	50	3.68×10^{-4}	9.33 ± 0.02	2.94 ± 0.02	4.81 ± 0.08	6.78 ± 0.05	10.16 ± 0.13	0.04	this work
ISE	50	3.82×10^{-4}	9.36 ± 0.03	2.87 ± 0.02	4.77 ± 0.10	6.72 ± 0.04	10.20 ± 0.10	0.08	this work
	15	7.22×10^{-3}	9.32 ± 0.04	2.84 ± 0.05	4.81 ± 0.12	6.80 ± 0.07	10.12 ± 0.16	0.12	this work
	40	5.0×10^{-4}			5.2				[16]
	3	3.0×10^{-3}		2.65	4.88				[17]

tained when the electrode potential was tested at different pH values and fixed metal ion concentration.

Several $c(\text{L}_\text{T}):c(\text{M}_\text{T})$ ratios were used to test the electrode performance and to verify whether indeed one can employ the refinement procedure CFC II, which was used previously only for polarographic data [15]. Some of the ratios were quite low (much less than 20) and usually not suitable for the polarographic study of metal-ligand systems. Other ratios were higher, as one often is using in polarography. Some results obtained, in the form of ECFC (points) and TCFC (lines), are seen in Figure 4. Examples of the refined stability constants for different ratios are included in Table 2. It was pleasing to note that the modeling and refinement procedure designed and used for the treatment of polarographic data worked very well also for ISE. The complex formation curves obtained from ISE, as one would expect, were similar to those from DPP experiment. More gratifying was the fact that the stability constants obtained from ISE were within a typical, for this technique, experimental error similar to those from polarography. It is important to note that

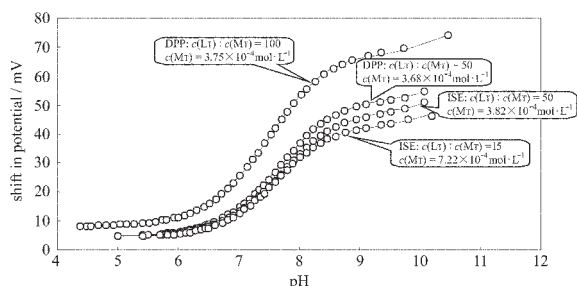


Fig.4 Experimental (data points) and theoretical (lines) complex formation curves (ECFC and TCFC) obtained for the refined stability constants and the metal-ligand model seen in Table 2.

only ML and ML_2 were reported [16,17] when ISE were employed in ligand titration, here all species found by DPP were confirmed by ISE. The correctness of the overall analytical procedure as well as the performance of the ISE were tested by analysis of the response of the ISE in the pH range studied. The response of ISE is towards the free metal ion concentration that is opposite to DPP, where the recorded current can be attributed to all species present in a solution. In Fig.5 the potential of ISE is plotted vs the free metal ion concentration. The free ion concentration was calculated for each pH value from mass-balance equations containing the refined stability constants for the model proposed in this paper. It is seen that the electrode response was linear down to the free metal ion concentration $5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. Note that the total metal ion concentration $c(\text{MT})$ did not change significantly during the experiments. The relationship seen in Fig.5 indicates that there was not a significant change in the electrode response in time (a single experiment lasts several hours) as well as with a change in the pH.

It is seen from equation 2 that the slope is an

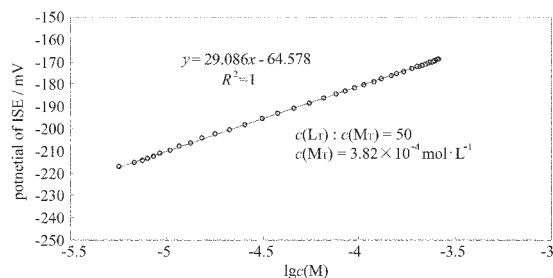


Fig.5 Variation in the potential of ISE vs the calculated free metal ion concentration obtained from mass-balance equations containing the proposed model and the refined stability constants.

important parameter in the refinement procedures. Initially, the slope obtained from the calibration of ISE was used to compute the stability constants with standard deviations as well as the standard deviation in the overall fit of the TCFC into ECFC. Next, the slope was slightly varied (upwards or downwards) and a new set of refined values together with the overall fit was obtained. The final values of stability constants were estimated with the iteratively calculated slope that generated the best fit of the TCFC into the ECFC. The iteratively calculated and used in a final refinement procedure slope for $c(L_T):c(M_T)$ ratio 50 is seen in Fig. 5. The refined slopes did not differ by much from obtained in the calibration operation of ISE. However, the difference could be regarded as significant, when the calibration of ISE was obtained in a broad concentration range of the standard cadmium solutions. When one assumes that the electrode response should be linear throughout the experiment then the refined slope value seems to be the appropriate one to use.

3.3 Species Distribution Diagram

The species distribution diagram for cadmium-glycinamide system is seen in Fig.6. All metal species are formed in consecutive manner with a large fraction for ML, ML_3 , $ML_3(OH)$, and with a small fraction for ML_2 and MHL. The fraction of MHL does not vary much in the pH range between 4 and 6. This agrees well with an almost constant value in the DPP peak height seen in Fig.1. The small fraction of MHL and constancy in the solution composition in this pH range resulted in the very small change in the free metal ion concentration. Even though numerous data points were collected in that pH range, they did not vary in value much for DPP and ISE. It is seen in Fig.6 that the

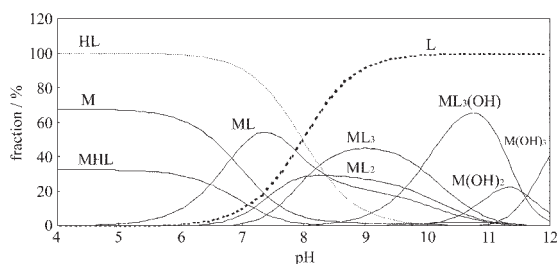


Fig.6 Species distribution diagram as a function of pH calculated for the Cd(II)-glycinamide system with the optimized stability constants reported in Table 2 at $c(M_T) = 3.75 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ and $c(L_T):c(M_T) = 50$.

metal species ML, ML_2 and ML_3 are formed in a consecutive fashion and there is not a pH range where one metal species is really a predominant one. This explains the continuity in the slope variation seen in Figures 2 and 3. Since the formation of ML_2 would occur to a small degree, significantly larger standard deviation was obtained for this complex when compared with values obtained for ML and ML_3 (see Table 2). Most of experiments were terminated at pH just above 10. This is why there were not enough experimental data for which the contribution of $ML_3(OH)$ to the readout (E_{ISE} or E_p) was substantial. Because of that slightly larger standard deviation in the calculated stability constant for this complex is observed in Table 2.

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