

ARTICLE

Determination of Stability Constants of Cadmium-Glycine Complexes by a Unified Treatment for Potentiometric and Polarographic Data

Jian-min Zhang*, Qiu-zhi Shi

Department of Chemistry, Zhengzhou University, Zhengzhou 450052, China

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The cadmium(II)-glycine system was studied by the two experimental techniques, ion sensitive electrode (ISE) and differential pulse polarography (DPP), and the experimental data obtained were used by a unified mathematical treatment to calculate the complex stability constants. The combination of the two techniques is of many advantages as ISE can be performed at low $[L_T]:[M_T]$ ratios and significantly higher $[M_T]$, whereas DPP could be used well at large $[L_T]:[M_T]$ ratios and much smaller $[M_T]$. This makes it possible to study a metal-ligand system in a relatively broader range of experimental conditions that, in turn, provides more information about the metal-ligand system of interest. Applying the unified mathematical treatment to the cadmium-glycine system, two new complexes MHL and $ML_2(OH)$ as well as three complexes ML, ML_2 and ML_3 , reported in literatures, could be modeled and all their stability constants have been refined.

Key words: Metal complex, Polarography, Potentiometry, Stability constant

I. INTRODUCTION

In the field of determination of metal complex stability constants, the experimental methods applied should be classified into two ways—an equilibrium technique and a dynamic technique [1]. The equilibrium technique, such as glass electrode potentiometry (GEP) and ion sensitive electrodes (ISE), means that the concentrations of all species presented in a sample are the same in bulk as well as at the surface of a sensor during the experimental process [2-6]. Polarography, or more generally voltammetry, is a dynamic technique as opposed to GEP or ISE that can be thought as a static electrochemical technique. While polarography/voltammetry is performed, 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. According to experimental phenomena during the reduction processes of metal complexes on the mercury electrode, metal complexes could be thought as three kinds—fully labile, non-labile and inert metal-ligand systems [7,8]. It has been shown recently that it is possible to evaluate stability constants of many metal complex systems [9-12] 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 [11,12] 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-glycine, was chosen to verify the validity of the proposed procedure.

II. EXPERIMENTAL

A. Materials and instruments

The ligand, glycine, was obtained from Aldrich, and all other reagents used were of analytical grade. The 0.1 mol/L stock solution of cadmium nitrate for the calibration of ISE was prepared in 0.01 mol/L 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 ± 0.1 mV (± 0.001 pH unit) with PHI 72 meters (Beckman). A combination glass electrode and a solid-state membrane cadmium ion sensitive 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 and 90 ms, respectively.

* Author to whom correspondence should be addressed. E-mail: zhjm@zzu.edu.cn

B. Procedures

In a typical run, the first polarogram was recorded for a solution containing about $5.00 \times 10^{-5} - 2.00 \times 10^{-4}$ mol/L of Cd(II) in 0.5 mol/L NaNO₃. Several different total-ligand to total-metal concentration ratios between 100–400 were used and were prepared by an addition of the appropriate amount of the solid ligand glycine 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, and after each addition a new polarogram was recorded. In this way a set of 40–50 polarograms were obtained for each [L_T]:[M_T] ratio as a function of pH. All polarograms were recorded on solutions with an ionic strength of 0.5 mol/L.

The experiments of ISE were done as the same procedure as polarography. 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 mol/L Cd²⁺ solution for at least 1 h. Two calibration procedures were tested before and after an experiment of metal complexes.

III. DATA TREATMENT

When metal complexes are consecutively formed in a solution sample, its polarographic peak usually shifts towards more negative potential and varies in height. For thermodynamically reversible processes, the shift in the peak potential and the variation in the peak height are described mathematically in terms of changes in the composition of the solution, when the experiment is performed at fixed [M_T]:[L_T] ratio and varying pH, by the following equation [11]

$$\begin{aligned} [E_P(M) - E_P(\text{comp})]_{\text{pH}} - \frac{RT}{nF} \ln \left[\frac{I_P(\text{comp})}{I_P(M)} \right]_{\text{pH}} \\ = \frac{RT}{nF} \ln \left(\frac{[M_T]}{[M]} \right)_{\text{pH}} \end{aligned} \quad (1)$$

where $E_P(M)$ and $E_P(\text{comp})$ stand for the peak potential in the absence and the presence of metal complexes, respectively, $I_P(M)$ and $I_P(\text{comp})$ stand for the peak current in the absence and the presence of metal complexes, respectively, [M_T] and [M] stand for the (free) metal ion concentration in the absence and the presence of metal complexes, respectively.

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 [13]

$$[E_P(M) - E_P(\text{comp})]_{\text{pH}} = \text{SLOPE} \ln \left(\frac{[M_T]}{[M]} \right)_{\text{pH}} \quad (2)$$

where $E(M)$ 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 [M_T]:[L_T] ratio.

The right-hand sides of equations (1) and (2) contain the total and free metal ion concentrations. 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, however, could be calculated from mass-balance equations written for the assumed model. Graphs of values of the right-hand sides of equations (1) and (2) *vs.* pH are usually called theoretical complex formation curves (TCFC).

The mass-balance equations are written for the assumed metal-ligand model that should include the complexes for calculated stability constants, M_xL_yH_z, M_xL_y, and M_xL_y(OH)_z, and the complexes for known stability constants, M_x(OH)_y and H_xL_y.

$$\begin{aligned} [M_T] = [M] + \sum \sum x [M_x(\text{OH})_y] \\ + \sum \sum \sum x [M_x L_y H_z] + \sum \sum x [M_x L_y] \\ + \sum \sum \sum x [M_x L_y (\text{OH})_z] \end{aligned} \quad (3)$$

$$\begin{aligned} [L_T] = [L] + \sum \sum y [M_x L_y] \\ + \sum \sum \sum y [M_x L_y H_z] + \sum \sum y [M_x L_y] \\ + \sum \sum \sum y [M_x L_y (\text{OH})_z] \end{aligned} \quad (4)$$

For the cadmium-glycine system proposed in this work, equations (3) and (4) would become

$$\begin{aligned} [M_T] = [M] + \beta_{\text{MHL}} [M][H][L] + \beta_{\text{ML}} [M][L] \\ + \beta_{\text{ML}_2} [M][L]^2 + \beta_{\text{ML}_3} [M][L]^3 \\ + \beta_{\text{ML}_2(\text{OH})} [M][L]^2[\text{OH}] + \beta_{\text{M}(\text{OH})} [M][\text{OH}] \\ + \beta_{\text{M}(\text{OH})_2} [M][\text{OH}]^2 + \beta_{\text{M}(\text{OH})_3} [M][\text{OH}]^3 \\ + \beta_{\text{M}(\text{OH})_4} [M][\text{OH}]^4 + 2\beta_{\text{M}_2(\text{OH})} [M]^2[\text{OH}] \\ + 4\beta_{\text{M}_4(\text{OH})_4} [M]^4[\text{OH}]^4 \end{aligned} \quad (5)$$

$$\begin{aligned} [L_T] = [L] + \beta_{\text{HL}} [H][L] + \beta_{\text{H}_2\text{L}} [H]^2[L] \\ + \beta_{\text{MHL}} [M][H][L] + \beta_{\text{ML}} [M][L] \\ + 2\beta_{\text{ML}_2} [M][L]^2 + 3\beta_{\text{ML}_3} [M][L]^3 \\ + 2\beta_{\text{ML}_2(\text{OH})} [M][L]^2[\text{OH}] \end{aligned} \quad (6)$$

The stability constants of metal complexes that would be refined by fitting the TCFC into the ECFC are

marked as bold. The mass-balance equations (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, dissociation constant of water and hydrolysis constants for cadmium (Table I) 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.

TABLE I Overall stability constants for Cd(II) complexes with OH^- , protonation constants for the ligand glycine(L) and dissociation constant of water (all from [14]) included in the Cd-L-OH model and used in the refinement procedure for DPP and ISE data.

| Equilibrium | $\log\beta$ |
|--|-------------|
| $\text{Cd}^{2+} + \text{OH}^- = \text{Cd}(\text{OH})^+$ | 4.0 |
| $\text{Cd}^{2+} + 2\text{OH}^- = \text{Cd}(\text{OH})_2$ | 7.7 |
| $\text{Cd}^{2+} + 3\text{OH}^- = \text{Cd}(\text{OH})_3^-$ | 10.3 |
| $\text{Cd}^{2+} + 4\text{OH}^- = \text{Cd}(\text{OH})_4^{2-}$ | 12.0 |
| $2\text{Cd}^{2+} + \text{OH}^- = \text{Cd}_2(\text{OH})^{3+}$ | 5.06 |
| $4\text{Cd}^{2+} + 4\text{OH}^- = \text{Cd}_4(\text{OH})_4^{4+}$ | 24.9 |
| $\text{H}^+ + \text{L}^- = \text{HL}$ | 2.41 |
| $\text{HL} + \text{H}^+ = \text{H}_2\text{L}^+$ | 9.57 |
| $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ | 13.78 |

IV. RESULTS AND DISCUSSION

A. Polarographic study

A set of differential pulse polarograms, recorded in the Cd(II)-glycine system as a function of pH, shows a single and well shaped DPP wave which peak width is about 62 mV, then the metal-ligand system is classified as fully labile [9] on the differential pulse polarographic time scale and its electrochemical reduction on mercury electrode could be considered as thermodynamically reversible processes [7,8]. Two relationships, observed shifts in DPP peak potential plotted *vs.* $\log[\text{L}]$ and 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.1. The continuous change in the slope is observed with the solid line indicating the maximum value of about 90 mV per log 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.* $\log[\text{L}]$

should be 30, 60 and 90 mV/log[L], respectively. There is not a significant shift in the peak potential up to pH of about 6 (Fig.2). This might indicate the absence of cadmium complexes with glycine. However, one can not 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 10 the free ligand L predominates in a solution and one would not 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 10 (Fig.2). This indicates the formation of a metal complex containing OH group, $\text{ML}_2(\text{OH})$.

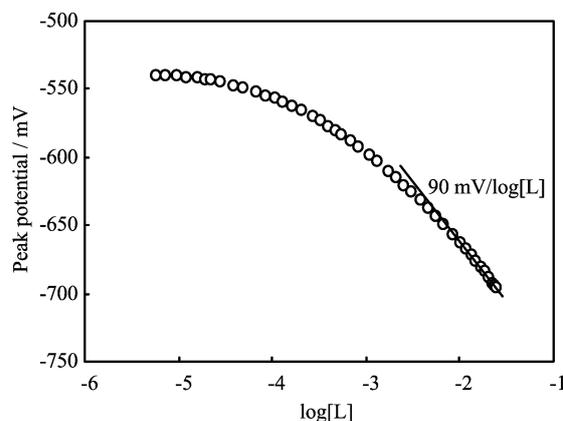


FIG. 1 Variation in DPP peak potential E_p for the Cd-glycine system as a function of the free ligand concentration at 25 °C and an ionic strength of 0.5 mol/L. All polarograms were recorded on one solution sample containing initially $[\text{M}_T]=1.55 \times 10^{-4}$ mol/L, $[\text{L}_T]:[\text{M}_T]=200$.

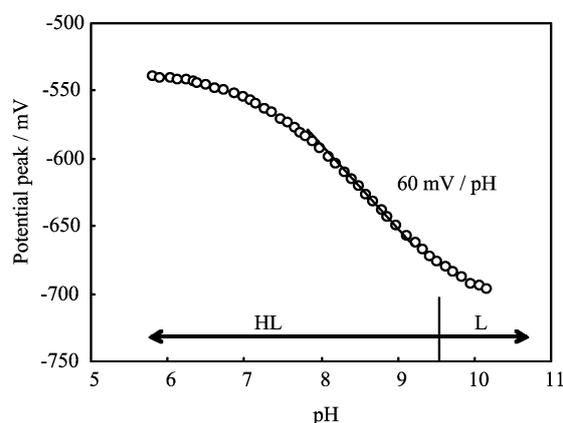


FIG. 2 Variation in DPP peak potential E_p for the Cd-glycine system as a function of pH (experimental parameters as in Fig.1).

From the above analysis of the shifts in the peak potential *vs.* $\log[\text{L}]$ and pH, it can be predicted that five cadmium complexes, MHL, ML, ML_2 , ML_3 and $\text{ML}_2(\text{OH})$, might be present in the cadmium-glycine

TABLE II Overall stability constants for Cd(II) with glycine refined in this work by DPP and ISE (using the same curve fitting procedure as described in the text) at 298 K and $\mu=0.5$ mol/L

| Exp. | Ratio | $[M_T]/(\text{mol/L})$ | $\log\beta$ | | | | | Ref. |
|------|-------|------------------------|-----------------|-----------------|-----------------|------------------|-------------------|-----------|
| | | | MHL | ML | ML_2 | ML_3 | $ML_2(\text{OH})$ | |
| DPP | 400 | 8.35×10^{-5} | 9.78 ± 0.11 | 4.37 ± 0.03 | 7.85 ± 0.04 | 10.11 ± 0.03 | 11.53 ± 0.10 | This work |
| | 200 | 1.55×10^{-4} | 9.67 ± 0.15 | 4.35 ± 0.02 | 7.83 ± 0.03 | 10.03 ± 0.04 | 11.48 ± 0.13 | This work |
| | 100 | 2.55×10^{-4} | 9.62 ± 0.12 | 4.41 ± 0.02 | 7.81 ± 0.03 | 10.07 ± 0.05 | 11.46 ± 0.11 | This work |
| | | | | 4.24 ± 0.03 | 7.77 ± 0.08 | 10.00 ± 0.03 | | [14] |
| ISE | 100 | 2.55×10^{-4} | 9.73 ± 0.13 | 4.32 ± 0.03 | 7.72 ± 0.04 | 10.06 ± 0.04 | 11.52 ± 0.11 | This work |
| | 50 | 1.00×10^{-3} | 9.68 ± 0.11 | 4.28 ± 0.03 | 7.75 ± 0.03 | 10.02 ± 0.05 | 11.58 ± 0.10 | This work |
| | 20 | 1.00×10^{-3} | 9.65 ± 0.14 | 4.34 ± 0.02 | 7.82 ± 0.04 | 10.07 ± 0.06 | 11.53 ± 0.12 | This work |
| | 12 | 1.00×10^{-3} | 9.71 ± 0.14 | 4.32 ± 0.03 | 7.76 ± 0.05 | 10.04 ± 0.06 | 11.49 ± 0.13 | This work |
| | | | | 4.18 | 7.50 | 9.76 | | [14] |

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-glycine system studied. As examples, the ECFCs obtained at $[L_T]:[M_T]$ ratios of 400, 200 and 100 are seen in Fig.3 (circles). The theoretical complex formation curves (TCFCs) for the above model are also seen in Fig.3 (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 II. If the complexes MHL and $ML_2(\text{OH})$ 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.

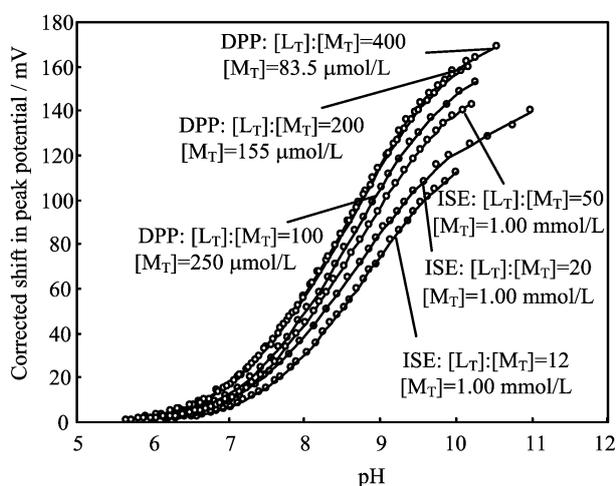


FIG. 3 Experimental (data points) and theoretical (lines) complex formation curves (ECFC and TCFC) obtained for the refined stability constants and the metal-ligand model seen in Table II.

B. ISE study

According to the manufacturer specification, the commercial ISE could be employed in a broad pH range (between 2 and 10) and a linear response down to about $1 \mu\text{mol/L}$ Cd(II). Since the experiments were performed at the total metal ion concentration between 1 and 0.1 mmol/L, the electrode response was tested only down to 0.001 mmol/L of Cd(II). 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 ± 0.4 mV.

Several $[L_T]:[M_T]$ 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. 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 Fig.3. Examples of the refined stability constants for different ratios are included in Table II. 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 well known that the response of ISE is towards the free metal ion concentration. In Fig.4 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 work. It is seen that the electrode response was linear down to

the free metal ion concentration 4 nmol/L. Note that the total metal ion concentration $[M_T]$ did not change significantly during the experiments. The relationship seen in Fig.4 also 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.

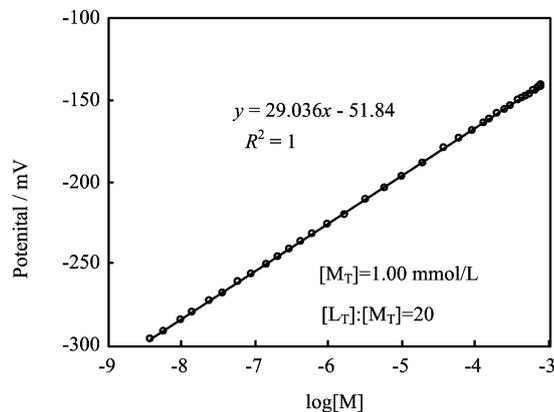


FIG. 4 Variation in the potential of ISE *vs.* the calculated free metal ion concentration obtained from mass-balance equations containing the proposed model and the refined stability constants.

It is seen from Eq.(2) that the slope is an 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 slope in a final refinement procedure for $[L_T]:[M_T]$ ratio 20 is seen in Fig.4. 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.

V. ACKNOWLEDGMENT

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