

# 利用络合物形成曲线设计金属络合物体系模型及优化络合物稳定常数

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## Modelling of Metal-Ligand System and Optimizing of Stability Constants by the Use of Polarographic Complex Formation Curves

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In this paper the Bi(III)-ligand(pyridine-2-carboxylic acid) system was studied by direct current sampled polarography (DC\_TAST) at a fixed ratio of total-ligand to total-metal concentration and changing pH. The polarographic experimental complex formation curve (ECFC) and the theoretical complex formation curve (TCFC) were used for modelling the metal-ligand system and optimizing stability constants. The ECFC, in which experimental parameters of polarography are included (a shift in a half-wave potential and a variation in a diffusion controlled limiting current), appears to be a characteristic function for a particular metal-ligand system. The TCFC is a theoretical curve calculated for the designed metal-ligand model from mass-balance equation. Five bismuth complexes MHL, ML, ML<sub>2</sub>, ML<sub>3</sub> and ML<sub>3</sub>(OH) with their stability constants as  $\log \beta$  7.54 ± 0.10, 7.50 ± 0.02, 13.91 ± 0.04, 18.15 ± 0.03 and 26.75 ± 0.02, respectively, are reported.

Keywords: metal complex system stability constant computer analytical program bismuth  
pyridine-2-carboxylic acid

## 0 Introduction

Polarography is an important modern analytical technique that is widely applied in many scientific fields, such as environment and biomedical engineering. Polarography, however, is seldom used in speciation studies of metal-ligand complex system. In all stability constants reported in the literature<sup>[1]</sup>, polaro-

graphic results contribute a fraction of one percent to all formation constants included. The reason may lie on that electrochemists concentrated mainly on theories of processes occurring at the working electrode in the presence of ligands<sup>[2,3]</sup> rather than on working out simple and reliable analytical procedures for speciation by polarography which could be successfully used by non-electrochemists. This, in addition, resulted in a

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lack of appropriate software which would directly use polarographic data for formation constant calculations. It is well known that glass electrode potentiometry (GEP) is an analytical method that is most frequently applied in the metal-ligand equilibria study. GEP, however, cannot be used for speciation studies of relatively strong complexes of very acidic metal ions such as Bi (III) and relatively weak complexes of metal ions, such as Pb (II). The former has to be studied at extremely low pH and both these metal ions often require a large ligand-to-metal ratio and a low total metal ion concentration to suppress metal ion hydrolysis. The above mentioned requirements can usually be met by polarography without a problem. In the paper the bismuth-ligand (pyridine-2-carboxylic acid) system was studied by direct sampled polarography (DC\_TAST) at a fixed ratio of total-ligand to total-metal concentration and changing pH. The graph of the experimental corrected shift in half-wave potential versus pH is determined as the experimental complex formation curve that should be a characteristic function for a particular metal-ligand system. Using the computer analytical software specially written for treatment of polarographic data, stability constants of the bismuth-ligand system were refined by fitting experimental complex formation curve.

## 1 Experimental

The ligand, pyridine-2-carboxylic acid, was obtained from Aldrich, and all other reagents used were of analytical grade. All experiments were performed in a jacketed glass vessel, equipped with a magnetic stirrer, and thermostatic control at 298K by water circulating from a constant temperature bath. The pH of solution was measured to  $\pm 0.001$  pH unit with a PHI 72 meter and combination glass electrode (both Beckman). Direct sampled 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 2s. A silver/silver chloride electrode and a platinum electrode were used as reference and auxiliary

electrodes, respectively.

In a typical run, the first polarogram was recorded for a solution containing about  $5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  of Bi (III) in  $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ . 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 to the vessel containing a metal 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 0.01mL, and after each addition a new polarogram was recorded. In this way a set of 30 ~ 40 polarograms were obtained for each  $L_{\text{total}}: M_{\text{total}}$  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 increasing ionic strength of  $0.5 \text{ mol} \cdot \text{L}^{-1}$ .

## 2 Results and Discussions

A set of direct current sampled polarograms, recorded in the Bi (III) -ligand(pyridine-2-carboxylic acid) system as a function of pH, shows a single and well shaped DC\_TAST wave. The Bi (III) -ligand system is then classified as fully labile on the DC\_TAST time scale<sup>[4,5]</sup>. The single DC\_TAST wave represents all metal species present at a particular pH, and its half-wave potential shifts with the pH increase are shown in Fig. 1. In general, the shift in the half-wave potential plotted against pH can be used for the prediction of the formation of metal species. It has been demonstrated<sup>[6]</sup> that when one metal species is predominant in the pH range where one form of a ligand is also a predominant ligand species, then a slope of about  $m \times 59.16/n$  mV per pH unit should be observed at 25°C ( $m$  and  $n$  stand for the number of protons and electrons, respectively, involved in the electrochemical reaction). For example, in the pH range 1.2 ~ 3.1 the slope of 38mV/pH clearly indicates that  $\text{BiL}_2^+$  should be the major species, according to the following electrochemical reaction.

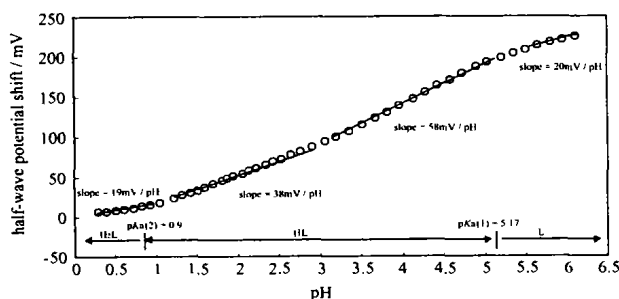


Fig. 1 Observed shift in the half-wave potential with pH for the Bi-ligand (pyridine-2-carboxylic acid) complex system at 25°C and an ionic strength of  $0.5 \text{ mol} \cdot \text{L}^{-1}$  ( $\text{NaNO}_3$ ). All polarograms were recorded on one solution sample containing initially  $[M_{\text{total}}] = 4.995 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ,  $[L_{\text{total}}]: [M_{\text{total}}] = 132$ .  $\text{pKa}(1)$  and  $\text{pKa}(2)$  are the protonation constants of the ligand pyridine-2-carboxylic acid.



From all slopes marked in Fig. 1, we can predict that five bismuth complexes,  $\text{MHL}$ ,  $\text{ML}$ ,  $\text{ML}_2$ ,  $\text{ML}_3$  and  $\text{ML}_3(\text{OH})$ , are present in the metal-ligand system. The shift in half-wave potential and the variation in diffusion controlled limiting current are described mathematically in terms of the changes in the composition of the solution by the following equation<sup>[7]</sup>:

$$\Delta E_{1/2}(i) - (RT/nF) \times \ln(I_d(M_{\text{comp}}(i)) / I_d(M_{\text{free}}(i))) = (RT/nF) \times \ln([M_{\text{total}}(i)] / [M_{\text{free}}(i)]) \quad (2)$$

where  $\Delta E_{1/2}(i)$  represents the shift in half-wave potential observed from the DC\_TAST experiment at each  $i$ th  $\text{pH}(i)$  value to which the metal-ligand system was adjusted in a polarographic cell,  $[M_{\text{total}}(i)]$  and  $[M_{\text{free}}(i)]$  are the total and free metal ion concentration, respectively, at each  $i$ th  $\text{pH}(i)$  value,  $I_d(M_{\text{comp}}(i))$  is the diffusion controlled limiting current recorded at the  $i$ th  $\text{pH}(i)$  value and  $I_p(M_{\text{free}}(i))$  is the calculated diffusion controlled limiting current of the metal  $\text{M}(\text{aq})$  one would observed at the  $i$ th  $\text{pH}(i)$  value with the assumption that complexes of the metal  $\text{M}$  were not formed. The left-hand side of eqn(2), containing terms available from the polarographic experiment, is called the experimental corrected shift(ECS) in the half-wave potential.

$$F_E(\text{pH}) = \Delta E_{1/2}(i) - (RT/nF)$$

$$\times \ln(I_d(M_{\text{comp}}(i)) / I_d(M_{\text{free}}(i))) \quad (3)$$

A graph of the ECS in the half-wave potential versus pH, called an experimental complex formation curve (ECFC) for the metal-ligand system, should be characteristic for a particular metal-ligand system as a function of all metal species formed in the solution. The experimental corrected shift in the half-wave potential was calculated for each datum point from eqn (3) and plotted vs. pH to give the experimental complex formation curve for the bismuth-ligand(pyridine-2-carboxylic acid) system (circles in Fig. 2). The right-hand side of eqn(2) contains the total and free metal ion concentrations. The free metal ion concentration is not available from the DC\_TAST experiment but it can be calculated from the mass-balance equations written for the assumed metal-ligand model that should include the complexes for calculated stability constants,  $M_xL, H_x, M_xL, H_x$ , and  $M_xL, (OH)_x$ , and the complexes for known stability constants,  $M_x(OH)_y$ .

$$[M_{\text{total}}] = [M_{\text{free}}] + \sum \sum x[M_x(OH)_y] + \sum \sum \sum x[M_xL, H_x] + \sum \sum x[M_xL,] + \sum \sum \sum x[M_xL, (OH)_x] \quad (4)$$

$$[L_{\text{total}}] = [L_{\text{free}}] + \sum \sum y[H_xL_y] + \sum \sum \sum y[M_xL, H_x] + \sum \sum y[M_xL_y] + \sum \sum \sum y[M_xL, (OH)_x] \quad (5)$$

The mass-balance eqs (4) and (5) are solved by the computer program CFC-II specially written for treatment of polarographic data obtained from metal-ligand systems. The known constants, for example all known  $M_x(OH)_y$  complexes, are kept fixed during

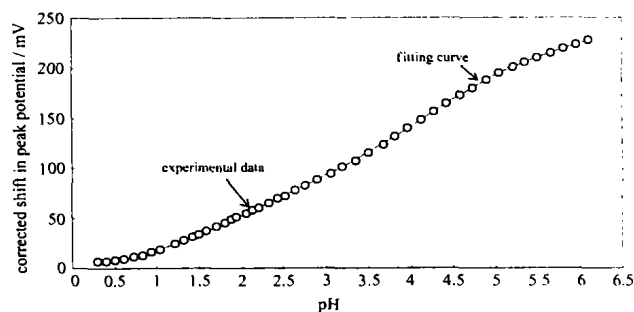


Fig. 2 Experimental and theoretical complex formation curves for the Bi-ligand(pyridine-2-carboxylic acid)-OH system (experimental parameters as in Fig. 1)

solution of mass-balance equations. The free metal ion concentration obtained from the mass-balance equations is used for the calculation of the right-hand side of eqn (2) for each pH value to which the sample was adjusted.

$F_T(\text{pH}) = (RT/nF) \ln([M_{\text{total}}(i)]/[M_{\text{free}}(i)])$  (6)  
A graphical representation of eqn (6) is called a theoretical complex formation curve (TCFC). Using the computer analytical program CFC-II, stability constants of metal complexes are refined till the TCFC fits the best ECFC (Fig. 2). The stability constants as  $\log \beta$  for five bismuth complexes MHL, ML,  $\text{ML}_2$ ,  $\text{ML}_3$  and  $\text{ML}_3(\text{OH})$  are finally obtained to be  $7.54 \pm 0.10$ ,  $7.50 \pm 0.02$ ,  $13.91 \pm 0.04$ ,  $18.15 \pm 0.03$  and  $26.75 \pm 0.02$ , respectively.

### 3 Conclusions

The method and mathematical model described in this paper is a generalized approach in the stability constant calculation for metal complex systems. It allows the incorporation into the metal-ligand system any number of metal complexes, those which are known ( $\text{M}_x(\text{OH})_y$  and  $\text{H}_n\text{L}$ ) and those which are thought to be formed ( $\text{M}_x\text{L}_y\text{H}_z$ ,  $\text{M}_x\text{L}_y$ , and  $\text{M}_x\text{L}_y(\text{OH})_z$ ) and for which formation constants are calculated. As a test of this method, the Bi (III)-ligand(pyridine-2-carboxylic

acid) system was studied at a fixed ratio of total-ligand to total-metal concentration and changing pH. The polarographic experimental complex formation curve (ECFC) and the theoretical complex formation curve (TCFC) were used for modelling the metal-ligand system and optimizing stability constants. Five bismuth complexes MHL, ML,  $\text{ML}_2$ ,  $\text{ML}_3$  and  $\text{ML}_3(\text{OH})$  with their stability constants as  $\log \beta$   $7.54 \pm 0.10$ ,  $7.50 \pm 0.02$ ,  $13.91 \pm 0.04$ ,  $18.15 \pm 0.03$  and  $26.75 \pm 0.02$ , respectively, are reported.

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