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Determination of Stability Constants of Bis(biacetylmonoxime)-Ethylene Diimine and its *o*-methyl Ether Derivative with Pb(II) and Cd(II) using Differential Pulse Anodic Stripping Voltammetry

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Differential pulse anodic stripping voltammetry (DPASV) has been used for determination of the stability constants of bis(biacetylmonoxime) ethylene diimine (H_2EO) and bis(biacetylmonoxime) *o*-methylether-ethylenediimine ($EOMe_2$) with Pb(II) and Cd(II). The applicability of DPASV for stability constant determination of these complexes regarding complex stoichiometry and complex reduction was tested experimentally. It has been found that the conditional stability constants of these complexes are relatively low ($K' = 10^4 - 10^6$), and that complexes with $EOMe_2$ are ten times more stable those with H_2EO.

INTRODUCTION

The dioxime ligands bis(biacetylmonoxime) ethylene diimine (H_2EO) and its *o*-methylated dioxime derivative ($EOMe_2$) have the potential to act as tetradentate ligands through their four azomethine nitrogen atoms[1]. Complexes of these ligands with several transition elements have been reported, and it has been established that these ligands coordinate to metal ions through their four nitrogens. Ligands of this type can be used as models for porphyrins and vitamin B_{12},[2] and thus the degree of interaction of these ligands with toxic metals such as Pb(II) and Cd(II) might shed some light into the mechanism in which these metals interfere in the biological systems in case of exposure.

Many methods are available for investigating metal-organic interactions. These include: potentiometry, spectroscopy, polarography and others. Each technique has its own advantages and limitations which must be recognized before applying it to a certain system. Differential pulse anodic stripping voltammetry (DPASV) has been used by many workers to investigate metal-organic interactions, taking advantage of its high sensitivity and high detection limit[3–6]. This method is based on data obtained from a complexometric titration followed with differential pulse anodic stripping voltammetry, which permits the estimation of conditional formation constants of metal complexes. The method is applicable for 1 : 1

complexes that are not reduced at the same potential at which the uncomplexed metal ion reduction occurs.

In this work, DPASV has been applied for determination of conditional stability constants of H_2EO and $EOMe_2$ with Pb(II) and Cd(II). These ligands are known to form 1 : 1 complexes through their four azomethine nitrogens.[7] The complex reduction potential and its separation from that of the free metal ion were tested experimentally.

EXPERIMENTAL

The ligands H_2EO and $EOMe_2$ were prepared according to literature procedures[8,9]. All reagents used were of analytical grade. The supporting electrolyte was a 0.50 M sodium perchlorate solution. Dexygenation of nitrogen was achieved by passing it through a solution containing 2.5 g ammonium metavanadate dissolved in 250 ml of 1 M HCl over zinc amalgam.

Measurements were made in a universal titration cell containing 25.0 ml solution. The cell was mounted on a Metrohm Polarography Stand model 505. The working electrode was hanging mercury drop electrode. A silver/silver chloride reference electrode and a platinum counter electrode completed the three-electrode system. Polarograms were recorded on a Metrohm Polarecord model 626.

Procedure

25.0 Ml of 0.50 M sodium perchlorate solution was pipetted into the titration vessel. The ligand (H_2EO or $EOMe_2$) was then added to give an exact concentration in the range of about 10^{-5} M. Nitrogen was then bubbled for 8 minutes through the solution, then the stream of nitrogen was passed over the solution instead of being bubbled through it. Different metal ion (Pb(II) or Cd(II)) concentrations, to cover the titration curve before and after the equivalence point were added. After each metal ion addition, measurement was carried out by electrodeposition of the free metal ion into a hanging mercury drop for 50 seconds while stirring the solution, followed by a 15 second rest period, after which the differential pulse stripping scan was recorded for the quiet solution. The deposition potentials used were –0.45 and –0.60 V vs. Ag/AgCl electrode for the titration of H_2EO and $EOMe_2$ with Pb(II) and Cd(II) respectively.

Theory of Conditional Constants Estimation using Differential Pulse Anodic Stripping Voltammetry

Shuman and Woodward[6] applied DPASV to estimate the conditional stability constants of 1 : 1 complexes in aqueous solutions. The reaction between a metal ion M with a ligand L to form a 1 : 1 complex can be represented by the equation:

$$M^{n+} + L \underset{K_f}{\overset{K_r}{\rightleftharpoons}} ML^{n+} \tag{1}$$

with the conditional formation constant K'_{ML} defined as:

$$K' = \frac{[ML]}{[M]\,[L]} \tag{2}$$

where [ML], [M] and [L] represent the equilibrium concentrations of ML, M and L respectively. k_f and k_r are the kinetic rate constants of the forward and backward reactions. Provided that K'_{ML} is large or k_r is small, a pre-electrolysis potential could be found at which M and not ML is reduced to M(Hg) according to the reaction:

$$M^{n+} + ne = M(Hg) \tag{3}$$

The anodic stripping current i_a is proportional to the equilibrium concentration of uncomplexed metal ion:

$$i_a = \kappa[M^{n+}] \tag{4}$$

where κ is a constant that depends on the mercury electrode geometry and its volume, stirring efficiency, length of pre-electrolysis time, scan rate, and the diffusion coefficient of the metal both in solution and mercury. By mass balance:

$$[ML^{n+}] = C_M - \frac{i_a}{\kappa} \tag{5}$$

and

$$[L] = C_L - C_M + \frac{i_a}{\kappa} \tag{6}$$

where C_L and C_M represent the analytical molar concentrations of the ligand and the metal respectively.

Substituting equations (5) and (6) in equation (2) results in:

$$K'_{ML} = \frac{C_M - \frac{i_a}{\kappa}}{\frac{i_a}{\kappa}\left(C_L - C_M + \frac{i_a}{\kappa}\right)} \tag{7}$$

In the titration of L with a metal ion M, two regions in the titration curve can be identified. One before the equivalence point is reached, when $C_L > C_M$ and $[M^{+n}] = i_a/\kappa << C_M < C_L$ and equation (7) becomes

$$K'_{ML} \sim \frac{C_M}{\left(\frac{i_a}{\kappa}\right)(C_L - C_M)} \tag{8}$$

Thus, plotting i_a vs. $C_M/C_L - C_M$ will give a straight line with a slope $S_1 = \kappa/K'_{ML}$. The other region is well after the equivalence point, when $C_M >> C_L$

and the currents approach $i_a = \kappa(C_M - C_L)$. Plotting i_a vs. C_M should give a straight line with a slope $S_2 = \kappa$. Dividing S_2 by S_1 will give an estimate of K'_{ML}.

RESULTS AND DISCUSSION

Supporting electrolyte

The supporting electrolyte used in these measurements was a sodium perchlorate solution, since ClO_4^- is known not to form complexes with metal ions, and thus interferences resulting from complex formation with the supporting electrolyte were eliminated. Titrations were performed at the pH of mixing (pH=8). Highly acidic solutions were avoided to prevent protonation of the donating nitrogen atoms. Highly basic solutions were also avoided, since they cause ligand hydrolysis.

Complex stoichiometry

Determination of conditional stability constants by DPASV using Shuman and Wooward method[6] can only be applied for 1 : 1 complexes. The two ligands H_2EO and $EOMe_2$ are known to form 1 : 1 complexes with metal ions by coordination through their four nitrogen atoms. DPASV can thus be applied for determination of the stability constants of these two ligands with Pb(II) and Cd(II).

Choice of plating potential

Current vs. potential curves were plotted for the free metal ion and for the 1 : 1 complexes with H_2EO and $EOMe_2$. The deposition potential chosen for each titration is the one at which the free metal gives a constant quantitative signal (as verified by the standard addition technique) and at which the 1 : 1 complex is not yet reduced. These potentials were found to be –0.45 and –0.60 V vs. Ag/AgCl electrode for the titration of Pb(II) and Cd(II) with H_2EO and $EOMe_2$ respectively (Fig. 1 and 2).

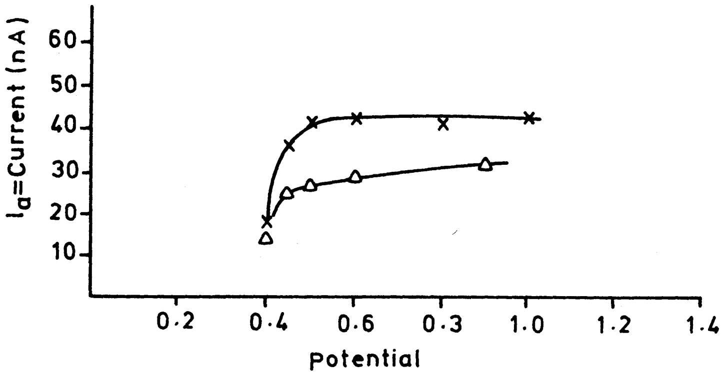

Fig. 1: Current-potential curves for free Pb(II), (x), and for its 1 : 1 complexes with H_2EO and $EOMe_2$, (Δ).
[Pb(II] = 4.0×10^{-5} M, [L] = 4.0×10^{-5} M

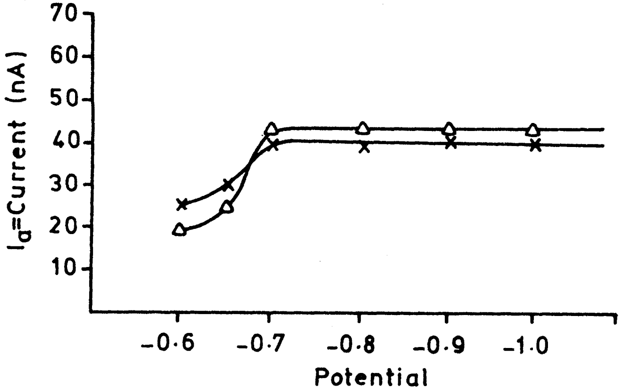

Fig. 2: Current-potential curves for free Cd(II), (x), and for its 1 : 1 complexes with H_2EO and $EOMe_2$, (Δ).
$[Cd(II)] = 4.0 \times 10^{-5}$ M, $[L] = 4.0 \times 10^{-5}$ M

Calculation of conditional stability constants

Tables 1–4 show the results of the titration of H_2EO and EOMe with Pb(II) and Cd(II) before and after the equivalence point. Before the equivalence point is reached, a plot of the stripping current i_a vs. $C_M/C_L - C_M$ gave a straight line with a slope of κ/K'_{ML}. After the equivalence point, where $C_M > C_L$, a plot of i_a vs. C_M gave a straight line with a slope equal to κ. The conditional stability constant K'_{ML} was then calculated from S_2/S_1. Values of K'_{ML} for the four studied complexes are shows in Table 5. In these calculations, the backward kinetic dissociation of the complexes was neglected.

TABLE 1

RESULTS FOR THE TITRATION OF H_2EO WITH Pb(II)

$C_L = 8.0 \times 10^{-5}$ M, U = −0.45 V vs. Ag/AgCl electrode

A. Before the equivalence point

$C_M/C_L - C_M$	i_a (μ_A)
0.25	0.021
0.50	0.029
1.00	0.046
1.50	0.065

Slope $S_1 = 0.0352$

B. After the equivalence point

$C_M \times 10^{-4}$	i_a (μ_A)
1.15	0.110
1.54	0.160
1.92	0.178
3.55	0.368

Slope $S_2 = 1.06 \times 10^3$; $K'_{ML} = 3.0 \times 10^4$

TABLE 2

RESULTS FOR THE TITRATION OF H_2EO WITH Cd(II)

$C_L = 8.0 \times 10^{-5}$ M, U = −0.60 V vs. Ag/AgCl electrode

A. Before the equivalence point

$C_M/C_L - C_M$	i_a (μ_A)
0.25	0.0125
0.50	0.0199
1.00	0.0347
1.50	0.0490

Slope $S_1 = 0.02923$

B. After the equivalence point.

$C_M \times 10^{-4}$	i_a (μ_A)
1.6	0.129
3.2	0.280
3.8	0.350
5.6	0.480

Slope $S_2 = 7.940 \times 10^2$; $K'_{ML} = 2.71 \times 10^4$

TABLE 3

RESULTS FOR THE TITRATION OF $EOMe_2$ with Pb(II)

$C_L = 5.73 \times 10^{-5}$ M, U = −0.45 V vs. Ag/AgCl electrode

A. Before the equivalence point.

$C_M/C_L - C_M$	i_a (μ_A)
0.25	0.012
0.50	0.014
1.00	0.020
1.50	0.025

Slope $S_1 = 0.0106$

B. After the equivalence point.

$C \times 10^{-5}$	i_a (μ_A)
6.28	0.120
6.81	0.132
7.22	0.132
7.50	0.153

Slope $S_2 = 2.64 \times 10^3$; $K'_{ML} = 2.49 \times 10^5$

TABLE 4
RESULTS FOR THE TITRATION OF $EOMe_2$ WITH Cd(II)
$C_L = 8.89 \times 10^{-5}$, $U = -0.60$ V vs. Ag/AgCl electrode

A. Before the equivalence point.

$C_M/C_L - C_M$	i_a (μA)
0.25	0.0024
0.50	0.0047
1.00	0.0082
1.50	0.0120

Slope $S_2 = 0.00756$

B. After the equivalence point.

$C_M \times 10^{-4}$	i_a (μA)
1.60	0.129
3.20	0.280
3.80	0.350
5.66	0.480

Slope $S_2 = 8.68 \times 10^2$; $K'_{ML} = 1.15 \times 10^5$

TABLE 5
CONDITIONAL STABILITY CONSTANTS OF H_2EO AND $EOMe_2$ WITH Pb(II) AND Cd(II)

Metal	H_2EO	$EOMe_2$
Pb(II)	3.0×10^4	2.5×10^5
Cd(II)	2.7×10^4	1.2×10^5

The conditional stability constants of H_2EO and $EOMe_2$ with Pb(II) and Cd(II) are found to be relatively low and are ten times larger for $EOMe_2$ than for H_2EO complexes. This could indicate that the deciding factor in determining the stability of these complexes is the space available between the four binding nitrogens. The repulsion between the methyl groups in case of $EOMe_2$ could lead to an increase in this space, thus forming complexes with higher stability.

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