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Equilibria in Aqueous Cadmium-Chloroacetate-Glycinate Systems. A Convolution-Deconvolution Cyclic Voltammetric Study

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Summary. Stability constants and composition of cadmium-glycinate binary complexes were determined using cyclic voltammetry. Furthermore, binary and ternary complex equilibria for chloroacetates and glycinate with cadmium in 0.1 *M* aqueous KNO_3 at *pH* 10.4 and 298 K were investigated. Cadmium forms binary complexes with chloroacetates of low stability and ternary ones with chloroacetate-glycinate of significant stability.

Keywords. Cadmium; Glycinate; Chloroacetate; Complexes; Convolution-Deconvolution Technique.

Gleichgewichte in wäßrigen Cadmium-Chloroacetat-Glycinat-Systemen. Untersuchungen mittels zyklischer Voltammetrie

Zusammenfassung. Gleichgewichtskonstanten und Zusammensetzung binärer Cadmium-Glycinat-Komplexe wurden mittels zyklischer Voltammetrie bestimmt. Weiters wurden binäre und ternäre Gleichgewichte von Chloroacetaten und Glycinat mit Cadmium in 0.1 *M* KNO_3 bei *pH* 10.4 und 298 K untersucht. Cadmium bildet binäre Komplexe geringer Stabilität mit Chloroacetaten und ternäre Komplexe von beträchtlicher Stabilität mit Chloroacetaten und Glycinat.

Introduction

Binary and ternary complexes of cadmium with amino acids have attracted considerable attention due to their important applications in biological systems [1]. The overall formation constants of cadmium glycine binary and ternary complexes were determined polarographically [2–6]. Apart from this, there is no literature on the polarographic determination of the equilibria and stabilities of cadmium-chloroacetate-glycinate ternary complexes. Thus, one of the purposes of the present paper is to investigate equilibria and stabilities in aqueous solutions of the title system.

Stability constants for labile systems can be derived from the variation of polarographic half-wave potentials, $E_{1/2}$, as a function of free ligand concentration. Inherent problems in DC polarography were partly overcome on using differential pulse techniques [7]. Recently, the convolution-deconvolution cyclic voltammetric procedure was found to be a better method for the determination of stability constants [8].

On the other hand, stability constants and composition of metal-ligand complexes have been determined by means of the POLAG Computer program from differential pulse polarographic data [13]. It is another purpose of the reported work to demonstrate the applicability of the POLAG program for the determination of composition and stability constants from convolution-deconvolution cyclic voltammetric data.

By the use of the mentioned method, the stability and composition of Cd-chloroacetate-glycinate binary and ternary complexes are estimated. The equilibria present in aqueous solutions are discussed.

Results and Discussion

It has been noted earlier that the most common method of determining stability constants of binary metal-ligand complexes (1) from polarographic data employs the approach given by *Deford* and *Hume* [14, 15]. The starting equations are:

$$\mathrm{m}M + \mathrm{n}L \rightarrow M_{\mathrm{m}}L_{\mathrm{n}}; \quad \mathrm{n} = 1, 2, \ldots, \mathrm{N}, \quad \mathrm{m} = 1, 2, \quad \beta_{\mathrm{mn}} = \frac{[M_{\mathrm{m}}L_{\mathrm{n}}]}{[M]^{\mathrm{m}}[L]^{n}} \qquad 1$$

$$\mathrm{m}M + \mathrm{n}L + \mathrm{p}L' \rightarrow M_{\mathrm{m}}L_{\mathrm{n}}L'_{\mathrm{p}}; \quad \mathrm{m}, \mathrm{n}, \mathrm{p} = 0, 1, 2, \ldots, \mathrm{N}$$

$$\beta_{\mathrm{mnp}} = \frac{[M_{\mathrm{m}}L_{\mathrm{n}}L'_{\mathrm{p}}]}{[M]^{\mathrm{m}}[L]^{\mathrm{n}}[L']^{\mathrm{p}}} \qquad 2$$

$$F = \exp[\mathrm{n}F/RT(E_{1/2(\mathrm{s})} - E_{1/2(\mathrm{c})})] = \ln(i_{\mathrm{ds}}/i_{\mathrm{dc}}) \qquad 3$$

$$F = 1 + C_l\beta_1 + C_l^2\beta_2 + \cdots + C_{\mathrm{L}}^{\mathrm{n}}\beta_{\mathrm{N}}, \qquad 4$$

where $E_{1/2}$ is the half-wave potential i_{d} is the diffusion current (the subscripts s and c refer to the uncomplexed and complexed metal ions, respectively) C_{L} is the analytical concentration of the ligand, and β_{N} is the overall stability constant of the Nth complex. For ternary complexes (2), the method of *Schaap* and *McMasters* [16, 17] is used in its original form or with modification [18]. The technique is based on the assumption that C_{L} and $C_{\mathrm{L'}} \gg C_{\mathrm{M}}$ ($C_{\mathrm{L'}}$ is the analytical concentration of the second ligand). The exact form of equation 4 is

$$F = 1 + [L]\beta_1 + [L]^2\beta_2 + \cdots + [L]^{\mathrm{n}}\beta_{\mathrm{N}} \qquad 5$$

which is derived from

$$F = C_{\mathrm{M}}/[L]. \qquad 6$$

The major problems encountered with the use of polarographic techniques are the difficulty in measuring current and half-wave potentials. It has been demonstrated that these problems can be partly solved by using differential pulse polarography [7]. A further disadvantage of all polarographic experiments is the use of only few current and potential values. It is preferable to use as many data points as possible. To satisfy these requirements, a transformation of the voltammetric current rather than the actual current is used. The transformation is performed by a convolution of the current with a $(\pi \mathrm{t})^{1/2}$ function.

$$I_1(t) = \int_0^t \frac{i(\mathrm{u})}{\sqrt{\pi(\mathrm{t} - \mathrm{u})}}\,\mathrm{du}, \qquad 7$$

where $i(\mathrm{u})$ is the current at time u and t is the total elapsed time [19, 20].

For reversible reduction of the systems in question, the polarographic data are replaced by the cyclic voltammetric convoluted ones with the notable advantage that all experimental data are utilized. On deconvolution, the action of the semidifferentiation operator on the convoluted current, $I_1(t)$, a quantity defined by $e = dI_1/dt$, is generated. The form of a cyclic deconvoluted current voltammogram is predicted to display a maximum, dI_{pc}, and a minimum, dI_{pa}, occurring at potentials E_{pc} and E_{pa} (where E_{pc} and E_{pa} are the peak current potentials in the cathodic and anodic scans, respectively), each equal to the polarographic half-wave potential. A complete cyclic voltammetric wave exhibits two mirror-image peaks with a half-width of 90.53/n mV at 298 K [8]. The peak response was found to be similar to that of differential pulse polarography at small pulses.

On convolution of the cyclic voltammetric data, the well-known *Herovesky–Ilkovic* equation applied for a DC polarographic experiment is altered to

$$E = E_{1/2} + RT/nF \cdot \ln[(I_L - I_1)/I_1], \qquad 8$$

where I_L is the limiting value of the convoluted current and E, $E_{1/2}$, R, T and F have their usual significance. Consequently, equation 3 is replaced by

$$F = \exp[nF/RT(E_{1/2(s)} - E_{1/2(c)})] + \ln(I_{ds}/I_{dc}). \qquad 9$$

On the other hand, on deconvolution the value of $E_{1/2}$ is replaced by the potential at the maximum amplitude of dI_1/dt, E_{pc}, and I_1 by the corresponding dI_{pc}. Thus,

$$F = \exp[nF/RT\,(E_{pc(s)} - E_{pc(c)})] + \ln(dI_{pc(s)}/dI_{pc(c)}). \qquad 10$$

The overall stability constants β_N and n are determined graphically or numerically [8] based on equations 1, 8, and 9. It has been shown earlier that the reversible polarographic data can be processed by the POLAG Computer program to yield reliable estimates of the overall stability constants for binary and ternary complexes. POLAG is a non-linear least-squares iterative program that minimizes U, the sum of squares of residuals, *i.e.*

$$U = \sum_{i=1}^{J} (F_{calc} - F_{obs})^2, \qquad 11$$

where J is the number of data points, F_{obs} is given by equation 10 and represents the experimental data, and F_{calc} is obtained from equation 5. Thus, for given values of β_{mnp}, C_M, C_L, and $C_{L'}$, F_{calc} depends on the particular combination of m, n, and p and the values of β_{mnp}. Various equilibrium models may be fitted to the polarographic data simply by changing the input value for β_{mnp}. Thus, the convolution-deconvolution cyclic voltammetric data can be processed by the POLAG program for the determination of composition and stability constants of the binary and ternary complexes.

Cyclic voltammograms of aqueous solutions of cadmium and cadmium-glycinate, -monochloroacetate, and -dichloroacetate binary and ternary systems were recorded at 298 K, $pH = 10.4$ and constant ionic strength of 0.1 M KNO_3. They exhibit a well designed *cv* wave over the potential range under investigation (-0.40 to -1.00 Volts *vs.* Ag^+). Cadmium is reduced electrochemically in presence and absence of the subject ligands *via* a two-electron reversible and diffusion-controlled *cv* wave. The reversibility and diffusion-controlled nature are judged on the basis of the following criteria:

a) For each given system, the peak potential, E_p, and the anodic and cathodic peak potential separation, $E_p^a - E_p^c = 30 \pm 2\,\mathrm{mV}$, exhibit no change on variation of the scan rate v [21].

b) The cathodic and anodic peak potentials are symmetrical, as revealed from the width of the *cv* wave ($E_p - E_{p/2} = 28.5 \pm 1.5\,\mathrm{mV}$) [22].

c) The convoluted voltammogram for all systems under investigation is the same as that of the forward scan, and the current, I_1, more or less reaches the same plateau value I_L and consistently returns during the reverse half of the sweep to its initial (zero) value, regardless of the scan rate [8] (Fig. 1).

d) The deconvoluted cyclic voltammograms for the subject systems show two mirror-image peaks, *i.e.* $E_{pc} = E_{pa}$.

e) The half-width of the deconvoluted wave amounts to $46.2 \pm 2.3\,\mathrm{mV}$ which is consistent with the theoretical value expected for a two-electron reversible wave (45.26 mV at 298 K) [8].

f) The peak current i_p of all *cv* waves correlates with the square root of the scan rate $v^{1/2}$ with a correlation coefficient r of 0.997.

Binary Systems

Examination of the deconvoluted data indicates that the uncomplexed cadmium ion is reduced at $E_{pc} = -0.552\,\mathrm{V}$. Upon addition of the ligand (glycine, monochloro- or dichloroacetic acids), the *cv* wave shifts to more negative potentials. As the concentration of the ligand is increased, the maximum deconvoluted current potential, E_{pc}, increases to more negative values and the deconvoluted current, dI_{pc}, decreases relative to that of the uncomplexed one. This is indicative of complex

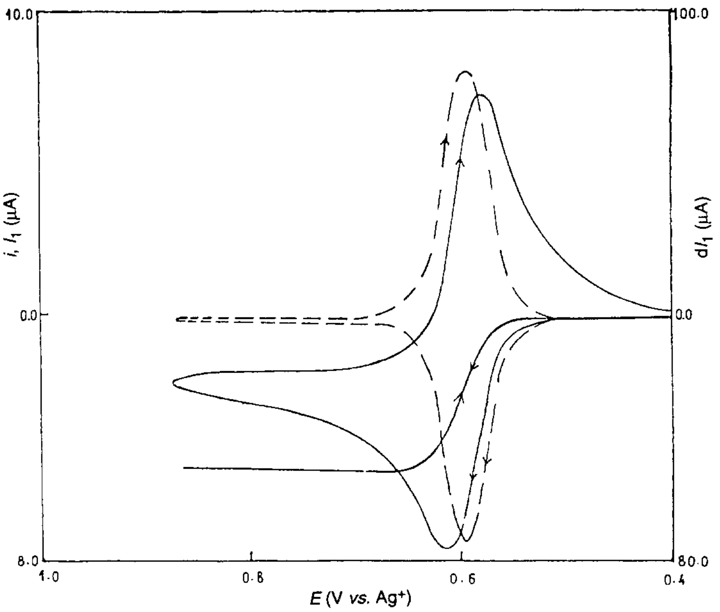

Fig. 1. Cyclic voltammograms of the cadmium-monochloroacetate binary complex: original (i), convoluted (I_1) and deconvoluted (dI_1) currents; $[Cd^{2+}] = 0.5\,\mathrm{mol \cdot dm^{-3}}$; [monochloroacetate] = $0.78\,\mathrm{mol \cdot dm^{-3}}$

formation. The decrease in current is interpreted as a result of decreasing the diffusion coefficient of the free solvated metal species in combination with a successive replacement of water molecules by more bulky ligand molecules. The overall stability constants logβ and the composition of the complexes are evaluated using the convolution-deconvolution data as input for the POLAG program. The best set of species is chosen according to the values of the statistical output of the program.

i) *Cadmium-glycinate*

Complexation of glycine with cadmium was studied at *pH* 10.4, demonstrating the applicability of the POLAG program for the determination of composition and stability constants of metal-ligand complexes using convolution-deconvolution data as input.

It is well known that glycinate functions as a bidentate NO ligand; five-membered metal chelates are assumed to be formed. Since the coordination number of cadmium is unlikely to exceed six, only binary species of type [CdL_n], [Cd$L_{(n-1)}$H$_j$] and [Cd$L_{(n-1)}$OH$_j$], where n = 1, 2, 3 and j = 1, 2, can be formed and tested. It is found that the hydrogen, hydroxo-, and polynuclear complex species show high statistical output (U, sum of squares of residual, and σ_{DATA}).

Table 1 comprises the most likely models. One can see that the model with single species ML_3 is rejected, since it has high U and σ_{DATA} values, and consideration of ML and ML_3 in the remaining models improve the results statistically. On the other hand, there is little choice between the other models. However, it appears that, according to $\sigma(\log\beta)$, the most likely model is ML_2 + ML_3. Comparing these results with those calculated by the graphical and numerical method ($\log\beta_2 = 7.74$ and $\log\beta_3 = 9.25$) [8], one can conclude that the processing of convoluted-deconvoluted cyclic voltammetric data by the POLAG program for the calculation of overall

Table 1. Stability constants of Cd-glycinate system

Model	logβ_1	logβ_2	logβ_3	$U \times 10^5$	$\sigma \times 10^3$
ML_3	–	–	9.67 (0.29)	41.46	7.69
ML + ML_3	6.79 (0.14)	–	11.25 (0.10)	0.25	2.42
ML_2 + ML_3	–	7.65 (0.13)	9.67 (0.09)	3.51	1.29
ML + ML_2 + ML_3	6.69 (0.49)	8.55 (0.19)	11.21 (0.30)	1.82	1.91
Reported Values					
	–	7.74	9.25 [8]		
	4.26	7.6 [9]			
	3.96	7.25 [10]			
	4.26	7.85	10.07 [11]		
	4.36	7.99	10.13 [12]		

stability constants is applicable. Furthermore, they show a reasonable good agreement with the reported ones. The difference is within the range of systematic error due to both experimental conditions and technique.

ii) *Cadmium-monochloroacetate*

A series of cyclic voltammograms has been recorded for solutions of cadmium (0.5 *M*) in presence of different concentrations of monochloroacetic acid (0.195–0.780 *M*) at *pH* 10.4 and 298 K. The peak potential, E_p, shifts to more negative values and the peak current, i_p, decreases on increasing the concentration of the ligand, indicating complex formation. The composition and stability constants of the binary complex formed are estimated on processing the convoluted-deconvoluted data obtained from the original *cv* data making use of the above mentioned procedure. It seems that the most possible model is the presence of a mixture of $[Cd(Cl{-}CH_2COO)]^+$ and $[Cd(Cl{-}CH_2COO)_2]$ along with the hydroxo species $[Cd(Cl{-}CH_2COO)OH]$ with overall stability constants of 1.31 ± 0.05, 1.87 ± 0.04, and -7.06 ± 0.09, respectively.

iii) *Cadmium-dichloroacetate*

Upon addition of successive amounts of dichloroacetic acid at *pH* 10.4 to a constant concentration of cadmium, a shift in the *cv* peak potential and a decrease in the peak current are observed. This is indicative of complex formation. Application of the POLAG program to the convoluted-deconvoluted data reveals that the most likely model corresponds to the presence of a $[CdCl_2{-}CHCOO]^+$ species. A stability constant of 0.96 ± 0.05 is estimated.

Ternary System

The ternary system is investigated by varying the concentration of glycine, gly, while the concentration of chloroacetates is kept constant at 0.10 *M* at 298 K and *pH* 10.4. The peak potential, E_{pc}, and the corresponding maximum deconvoluted current, dI_{pc}, are found to be more negative than in the absence of chloroacetates. This indicates the formation of ternary complexes. The overall stability constants and composition are determined as above. Various combinations of ternary complexes ($[Cd(glyL_{p-j}H_j)]$, $[Cd(glyL_{p-j}OH_j)]$, $[Cd(gly_2L_{p-j}H_j)]$, and $[Cd(gly_2L_{p-j}OH_j]$ where L is monochloroacetate or dichloroacetate, $p = 1, 2, 3, 4$ and $j = 0, 1, 2$) are proposed to be formed. Many models are rejected by large σ_{DATA} and U values or by large standard deviations of the stability constants. It is evident from the results that hydrogen, hydroxo-, and polynuclear ternary complex models are acceptable from their statistical output. This reveals that only simple ternary complexes of the types $[CdglyL_p]$ and $[Cdgly_2L_p]$ are probably present. Furthermore, it is evident that the most possible model for both cadmium-monochloroacetate-glycinate and cadmium-dichloroacetate-glycinate ternary complexes is the presence of a $[Cdgly_2L_2]$ species with overall stability constants of 10.49 ± 0.23 and 10.79 ± 0.25, respectively.

The stability of the ternary complex can be quantized by calculating the difference in the stability value $\log K$ for the reactions

$$\mathrm{Cdgly_2} + \mathrm{Cd}L'_2 \rightarrow \mathrm{Cdgly_2}L'_2 + \mathrm{Cd} \qquad 11$$

$$\log K = \log \beta_{\mathrm{Cdgly_2}L'_2} - \log \beta_{\mathrm{Cd}L'_2} \qquad 12$$

for the cadmium-monochloroacetate-glycinate complex and

$$\mathrm{Cdgly_2} + 2\mathrm{Cd}L' \rightarrow \mathrm{Cdgly_2}L'_2 + 2\mathrm{Cd} \qquad 13$$

$$\log K = \log \beta_{\mathrm{Cdgly_2}L'_2} - \log \beta_{\mathrm{Cdgly_2}} - 2 \log \beta_{\mathrm{Cd}L'} \qquad 14$$

for cadmium-dichloroacetate-glycinate complex. The values are found to be +0.973 and +0.928 for cadmium-monochloroacetate-glycinate and -dichloroacetate-glycinate, respectively. The positive values are indicative of a significant stabilization of ternary complexes with respect to the binary ones. Various equilibria involved in these binary and ternary systems (for monochloroacetate) are below with their equilibrium constants.

		$\log K$
(1)	$\mathrm{Cd} + L' \rightleftharpoons \mathrm{Cd}L'$	1.31
(2)	$\mathrm{Cd}L' + L' \rightleftharpoons \mathrm{Cd}L'_2$	0.56
(3)	$\mathrm{Cd} + 2\mathrm{gly} \rightleftharpoons \mathrm{Cdgly_2}$	7.65
(4)	$\mathrm{Cdgly_2} + \mathrm{gly} \rightleftharpoons \mathrm{Cdgly_3}$	2.02
(5)	$\mathrm{Cd} + 2\mathrm{gly} + 2L' \rightleftharpoons [\mathrm{Cdgly_2}L'_2]$	10.49
(6)	$\mathrm{Cd}L' + L' + 2\mathrm{gly} \rightleftharpoons [\mathrm{Cdgly_2}L'_2]$	9.18
(7)	$\mathrm{Cd}L'_2 + 2\mathrm{gly} \rightleftharpoons [\mathrm{Cdgly_2}L'_2]$	8.62
(8)	$\mathrm{Cdgly_2} + 2L' \rightleftharpoons [\mathrm{Cdgly_2}L'_2]$	2.85
(9)	$\mathrm{Cdgly_3} + 2L' \rightleftharpoons [\mathrm{Cdgly_2}L'_2] + \mathrm{gly}$	0.82

From the examination of these equilibria, one can conclude that the tendency of the binary complexes $[\mathrm{Cdgly_2}]$ or $[\mathrm{Cd}L'_2]$ to add the second ligand is comparable. The $\log K$ values are 2.85 and 8.62 for the addition of chloroacetate and glycinate, respectively. This confirms that the ternary complex formation is favoured. Furthermore, the complexing tendency of glycinate is much higher than that of chloroacetate (equilibria 7 and 8). These observations are in accordance with the weaker complexing nature of chloroacetate.

The present work demonstrates that the POLAG computer program can be used for the processing of convolution-deconvolution cyclic voltammetric data to evaluate the stability constants and composition of binary and ternary complexes in solution. This technique offers an advantage over the graphical and numerical procedure.

Experimental

Cadmium nitrate, potassium nitrate, glycine, mono- and di-chloroacetic acids were of AR BDH or Merck grade. Their solutions were prepared in fresh aqueous 0.1 *M* potassium nitrate solution as supporting electrolyte. The *pH* of the solutions was adjusted at 10.4 by potassium hydroxide and nitric acid solutions. Measurements at high *pH* values are comparatively insensitive to small *pH* errors. The subject ligands are present in the form of their conjugate base, *i.e.* glycinate and chloroacetates.

Cyclic voltammetric measurements were performed with a conventional three electrode cell configuration. An EG&G PAR model SMDE 303A mercury-drop system in the small hanging-drop mode was used as working electrode. The electrode area was 1.05×10^{-2} cm^2. The reference electrode was a Ag/AgNO$_3$ (0.01 M) electrode in 0.10 M KNO$_3$ solution. A platinum sheet of 1.0 cm^2 was used as an auxiliary electrode throughout. All experiments were performed at 298 K and the ionic strength was maintained at 0.2 M KNO$_3$. Solutions were purged with pure nitrogen before recording the voltammograms and an atmosphere of nitrogen was maintained above the working solution. The mercury-drop system was coupled with an EG&G PAR 173D Potentiostat/Galvanostat and a PAR 175 universal programmer. The system was interfaced with an AMSTRAD 1640 computer with mathematics coprocessor. The data were collected, stored and manipulated using the EG&G CONDECON 300 software. In all experiments 500 data points, equally spaced in time were acquired. Background data were substracted from the experimental data set, minimizing effects such as double layer charing currents. Internal resistance ohmic drop distortions were minimized by software compensation.

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