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STUDIES OF CADMIUM—ETHYLENEDIAMINE COMPLEX FORMATION IN SEAWATER BY COMPUTER-ASSISTED STRIPPING POLAROGRAPHY

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SUMMARY

An equation for stripping polarography is derived, relating the half-wave potential ($E^*_{1/2}$), ligand concentration, and dissociation constant of a complexed metal ion. This equation is similar to that for classical polarography, but contains an additional term which makes $E^*_{1/2}$ a linear function of the logarithm of the time. A computer-assisted system for generating stripping polarographic curves is also described. This system is used to characterize 10^{-8} M cadmium in a potassium nitrate solution and in sea water.

Current awareness of the importance of trace metals in natural waters has stimulated interest in the development of analytical techniques capable of determining the chemical speciation of these metals at levels of less than 10^{-8} M.

It has been shown experimentally [1] and theoretically [2—4] that trace metals in sea water exist in different forms. They may be complexed with simple inorganic ligands such as water, halides, carbonates, and sulfate, or by organic ligands such as amino acids, humic acids, sugars, carbohydrates and polymers. Their availability for biological and geochemical processes is largely determined by such species characteristics as oxidation state, degree of hydration, and complexation [5]. Because of the low levels at which these metals normally occur in the environment, direct determinations by classical methods cannot be made without prior concentration which usually modifies the species under investigation.

Classical d.c. polarography was one of the first analytical techniques capable of determining metal ion concentrations and speciation in aqueous solutions for levels of 10^{-5} to 10^{-7} M [6—8]. Numerous modifications of the classical method have been developed to increase sensitivity and also provide signals that are easier to measure. At present, one of the best methods for trace metal characterization is anodic stripping voltammetry (a.s.v.) [9, 10].

Stripping polarography is a variation on the normal a.s.v. technique. In stripping polarography, the peak stripping currents observed during the normal a.s.v. trace are plotted as a function of the deposition potential, so that a curve analogous to the classical d.c. polarogram is obtained (Fig. 1, a, b). The value at which the peak currents level off after the sharp rise and become

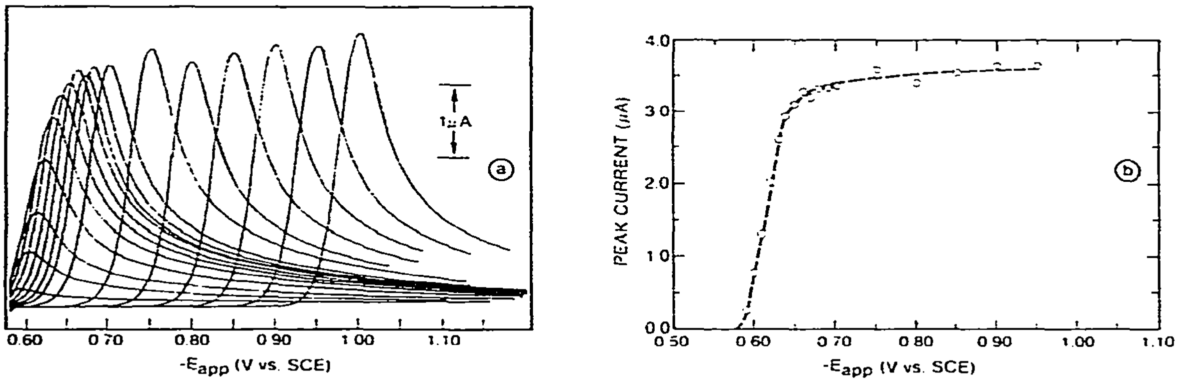


Fig. 1. (a) A.s.v. peaks obtained at each indicated applied potential; (b) stripping polarographic curve constructed from a.s.v. peaks (10^{-8} M cadmium(II) in sea water).

independent of the applied potential is known as the limiting current (i_{pl}). The potential at which the current is half the limiting current is the half-wave potential ($E^*_{1/2}$).

The method has been used for qualitative analysis of metals in natural waters at concentrations too low for direct polarographic analysis. Matson [11] and Fitzgerald [12], using the mercury composite graphite electrode (MCGE), suggested that the speciation of trace metals in sea water could be studied from peak current—electrolysis potential plots. However, Seitz et al. [13] demonstrated that deteriorating electrodes could alter the shape of these plots. Bubic and Branica [14] used stripping polarography with the hanging mercury drop electrode (HMDE) to establish that $Cd(H_2O)_6^{2+}$, $CdCl^+$ and $CdCl_2$ were the predominant species of cadmium in sea water. They did this by comparing values of the potential at the foot of the sigmoidal curve (E_p^*) obtained from natural sea water, with E_p^* observed for a model system.

Recently, Zirino and Kounaves [15] showed that for electrochemically reversible, simple-ion systems, the peak current—electrolysis potential relationships obtained by stripping polarography can be described by:

$$E = E^0 + \beta \ln [(i_{pl} - i_p)/i_p] + \beta \ln [2\delta_s r f_s/3D_s f_a] - \beta \ln(t) \qquad (1)$$

where E is the applied potential; E^0 the standard potential for the amalgam electrode; f_a and f_s are the activity coefficients for amalgam and simple ion; δ_s is the thickness of the diffusion layer; D_s the diffusion coefficient; r the radius of the mercury drop; t the electrolysis time; i_p the peak current; i_{pl} the peak current obtained under limiting conditons, and $\beta = RT/nF$, where R, T, n and F have their usual meanings.

This paper will show the derivation of the stripping polarographic relationship for an electrochemically reversible system containing a reagent which forms a complex with the depolarizer. The method is applied to studies of cadmium—ethylenediamine complexation in sea water by means of a computer-assisted system for generation of the curves.

THEORY

In the manner of the simple-ion relationship given earlier (15), the current is linearized over the electrolysis interval t, and it is assumed that $q = \bar{i}t$, where q is the charge accumulated over time t and $\bar{i}$ is the average current which flows over this period. However, for the complexed metal, $\bar{i}$ is controlled by the flux of complexed metal to the electrode and, from the mean value theorem [16],

$$\bar{i} = nFA\bar{F}_c \tag{2}$$

where $\bar{F}_c$ is the average flux of the complexed ion, A the area of the electrode and n and F have their usual meanings.

Similarly, when the bulk concentration of the complexed metal C_c is not significantly altered during electrolysis, the quantity $\bar{F}_c$ is proportional to $C_c - \bar{C}_c^0$ as given by the Nernst diffusion layer approximation

$$\bar{F}_c = (D_c/\delta_c)(C_c - \bar{C}_c^0) \tag{3}$$

where D_c is the diffusion coefficient of the complex, δ_c is the thickness of the diffusion layer, and $\bar{C}_c^0$ is the average concentration of the complex at the drop surface.

Combining these last three equations gives

$$q = nFA(D_c/\delta_c)(C_c - \bar{C}_c^0)t \tag{4}$$

At the limiting conditions, $\bar{C}_c^0 \to 0$, $q_l = nFA(D_c/\delta_c)C_c t$. Combining this with eqn. (4) gives

$$\bar{C}_c^0 = (q_l - q)/nFA(D_c/\delta_c)t \tag{5}$$

It is now assumed that the system is in equilibrium over the entire interval and that

$$K_c = (f_s C_s^0)(f_x C_x)^P / f_c C_c^0 \tag{6}$$

where K_c is the dissociation constant of the complex, f_c, f_x and f_s are activity coefficients of the complex, ligand and simple ion, respectively, P is the stoichiometric coefficient of the ligand with the metal ion, and C_x^0 is the concentration of ligand at the electrode surface. The following conditions are also assumed: (a) the solution contains a large excess of the complexing ligand compared to the complex, thus making the liberation of free ligand at the electrode surface, as the complex is reduced, insignificant, i.e. $C_x^0 = C_x$; (b) K_c is so small that the contribution of the simple ion to the overall current is negligible, i.e., $C_c \gg C_s$; (c) all activity coefficients remain constant over the interval.

Under these circumstances, use of the mean value theorem gives

$$\bar{C}_c^0 = (f_x C_x)^P f_s \bar{C}_s^0 / f_c K_c \tag{7}$$

Since the system is at equilibrium, the Nernst equation is obeyed at all times and at any instant of time

$$\theta = C_s^0 f_s / C_a^0 f_a = \exp\,[\beta^{-1}\,(E - E^0)] \qquad (8)$$

where C_a^0 is the concentration of the reduced metal at the surface of the drop and f_a is its activity coefficient. C_a^0 remains at present an unspecified function of t, thus $C_a^0 = f(t)$. Simplification of eqn. (8) gives $C_s^0 = \theta'\, f(t)$, and further application of the mean value theorem gives the average value of C_s^0

$$\bar{C}_s^0 = (\theta'/t) \int_0^t f(t)\,\mathrm{d}t \qquad (9)$$

But by definition, $\int_0^t f(t)\,\mathrm{d}t/t = \bar{C}_a$, and thus $\bar{C}_s^0/\bar{C}_a^0 = \theta'$, which means that the ratio of the average values is identical to the ratio of the instantaneous values.

The actual value of $\bar{C}_a^0$ is then obtained from the equation proposed for C_a^0 [17] under conditions of constant flux. Integrating again, and neglecting those terms not experimentally significant, gives

$$\bar{C}_a^0 = 3\bar{i}t/2nFAr = 3q/2nFAr \qquad (10)$$

Algebraically, use of the constant flux equation is justified because, by definition, $\bar{i}$ is constant over the entire interval. In actuality, this approximation introduces a small error at very low overvoltages and large values of t which is not experimentally resolvable under the usual a.s.v. conditions [15].

Substitution of the equivalent values for $\bar{C}_s^0$ and $\bar{C}_a^0$ in the Nernst expression gives

$$\bar{C}_s^0 = K_c(q_1 - q) fc/(C_x f_x)^P\, nFA(D_c/\delta_c)t \qquad (11)$$

As shown above

$$\bar{C}_s^0 f_s/\bar{C}_a^0 f_a = C_s^0 f_s/C_a^0 f_a = \exp\,[\beta^{-1}\,(E - E^0)] \qquad (12)$$

Substituting eqns. (10) and (11) into this equation gives

$$\exp\,[\beta^{-1}\,(E - E^0)] = [(q_1 - q)/q]\; 2\delta_c K_c f_c r/3(C_x f_x)^P f_a D_c t \qquad (13)$$

When $q = q_1/2$, the half-wave potential $E_{1/2}^*$ is obtained from

$$E_{1/2}^* = E^0 + \beta \ln\,[2\delta_c f_c r/3D_c f_a] + \beta \ln\,(K_c) - \beta P \ln\,(C_x f_x) - \beta \ln(t) \qquad (14)$$

Ordinarily, the ratio $\delta_c f_c/D_c$ for the complex is approximately equal to the ratio $\delta_s f_s/D_s$ for the simple ion. Thus the collection of terms $E^0 + \beta \ln\,[2\delta_s f_s r/3D_s f_a] - \beta \ln(t)$ is the half-wave potential for the simple ion ($E_{1/2s}^*$), and

$$E_{1/2c}^* = E_{1/2s}^* + \beta \ln\,(K_c) - \beta P \ln\,(C_x f_x) \qquad (15)$$

This result is similar to that for the classic polarographic wave of a complexed ion [18] but in addition, there is the linear dependency of $E_{1/2c}^*$ with $\ln(t)$.

Development of automated instrumentation for stripping polarography

It became apparent from preliminary efforts to confirm the theoretical relationships that obtaining the data points for the stripping polarographic curves required an excessive amount of time and effort. Each curve is composed from a minimum of 10—15 points, each point being at least one normal a.s.v. experiment. Under the best conditions, with deposition times of 10—30 min, the stripping polarographic curve would take at least 2 days, during which the operator has to monitor the instrument constantly, changing mercury drops and deposition potentials, and collecting output data.

Several workers [19—22] have demonstrated the utility of on-line computer systems for controlling electrochemical analysis. Since a large amount of data is produced by stripping polarography, interfacing with a computer also becomes extremely advantageous for the storage and evaluation of data. With the on-line computer, processing of data such as peak heights or integration of peak areas, can be done rapidly.

Interfacing of a computer with a commercial polarograph is relatively straightforward, and this technique was adopted to save time in the development of the necessary hardware and software. Within these constraints, a general, completely automated system for stripping polarography was developed. The system is extremely flexible and can be programmed to carry out any conceivable experiment of this type, with the experimental parameters selected by the user. The system can also accommodate other inputs such as pH and temperature sensors with only minor changes in hardware and software.

EXPERIMENTAL

Instrumentation

The computer used was a Hewlett-Packard 21MX (HP21MX) with 32K of RAM working memory and an HP disc drive for mass storage. In addition, the system contained 16 general-purpose I/O registers, a 91000A analog-to-digital 8-channel interface (A/D), and the ISA-FORTRAN extension software package for the above.

A Princeton Applied Research Polarographic Analyzer model 174A was used as the potentiostat. The electrolysis cell consisted of a PAR model 9323 HMDE fitted into a PAR model 9300 polarographic cell top, and a model 3343 cell bottom. The cell was not thermostated, but room temperature was maintained at 25 ± 1°C, and the cell temperature was continuously monitored. The solution was stirred with a 1.1-cm Teflon-covered stirring bar coupled to a Sargent-Welch 600-rpm synchronous-speed magnetic stirrer (model 576492). The reference electrode was a Markson model 1202 Ag/AgCl with a platinum-banded tip, which also served as the counter electrode. The PAR 174A was modified as described below.

Scan Control. The potential scan on the 174A is normally initiated by pressing the scan button, which disconnects the —15 V d.c. power to the ramp control circuit and allows the potential to start changing according to a preselected rate and direction. Modification for computer control consisted of providing the —15 V d.c. power through contacts on a relay, which in turn was controlled by bit 0 from the computer.

Cell control. Normally, the applied potential is controlled by a selector switch on the front panel. Even though this switch has only three positions (dummy cell on—off—cell on), it also simultaneously controls circuits for the summing amplifer, ramp generator, and potential feedback. Because of its many functions, this switch was replaced by a 10-contact relay connected in series with the selector switch. With the switch set to EXT (cell on), the cell can be turned on/off by the computer.

Initial potential selection. The initial deposition potential is normally selected by setting the initial potential control on the front panel of the 174A to the desired potential. For computer control, a digital-to-analog converter (D/A) was used to provide a controlled current to the 174A summing amplifier.

X-axis output voltage. A modification was required to the x-axis output circuit to provide the 0—10 V d.c. range necessary for operation of the HP21 A/D converter. The x-axis output, normally 0—1 V d.c., was increased by replacing resistor R118 on the programmer—potentiostat board by a 10 kohm variable resistor. It was then adjusted so that the x-axis output was 0—10 V d.c.

Stirrer control. The 174A does not provide any control for a stirrer. To provide for computer control, a solid-state relay was used. The state of bit 1 from the computer controls the 115-V a.c. power to the stirrer motor.

Gas control. The 174A does not provide any gas control. Nitrogen is normally used to purge the sample before an a.s.v. cycle and to maintain a gas blanket during the deposition and stripping steps. Gas control was achieved by addition of a solenoid-controlled three-way valve. The valve under computer control selects the purge or blanket outlet.

Drop dislodger and dispenser. To provide for the dislodging and dispensing of the mercury drop, a modified version of the PAR model 314 automated hanging mercury drop electrode (HMDE) was incorporated into the system (see Fig. 2). The Model 314 consists of a small metal enclosure that is mounted on the same stand as the cell and contains the stepper motor drive circuits and dislodge solenoid. The motor is a four-phase stepper type that rotates a precise number of degrees each time it is pulsed by its drive circuit. Reduction gears between the motor and the drive shaft set the drive shaft rotation at 0.25 degree per step. The drive circuits are controlled by 10-ms pulses provided by the computer. The duration and number of pulses can be specified in the control program.

Systems interconnections and operation

The system can basically be separated into three subsystems: (1) the HP21MX minicomputer; (2) the interfaces (IF1, IF2); and (3) the polarographic analyzer (PAR-174A). A block diagram of the system interconnections is shown in Fig. 3.

The HP21MX, apart from the CPU, includes a 16-bit I/O register and an A/D converter. The 16-bit output register provides a pathway for transferring data from the CPU to a peripheral device. Each of the 16 output lines can be set high (1) or low (0) by software control. The A/D converter (20-kHz A/D interface—HP91000A) is used for converting the x-axis (potential) and y-axis (current) outputs to digital form for manipulation and storage by the CPU.

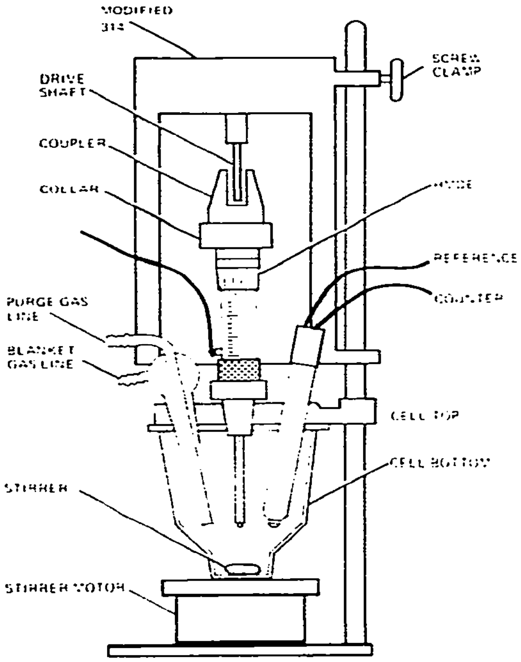


Fig. 2. Diagram of automated HMDE and cell.

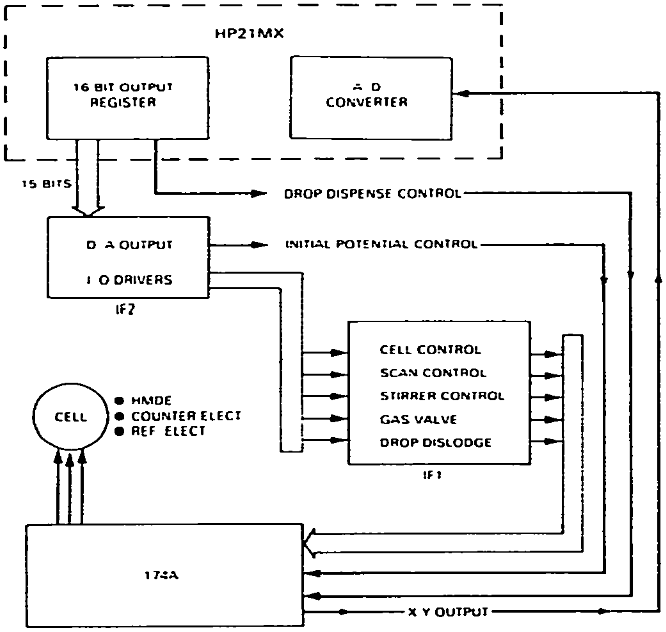


Fig. 3. Block diagram of automated system.

The A/D is directly connected to the x—y output posts on the rear panel of the 174A.

Two interface cards, IF1 and IF2, are located within the 174A. IF1 contains the cell control relay, stirrer control relay, scan control relay, voltage regulator, and gas control circuit. IF2 contains the D/A converter and the I/O drivers. The outputs from the 16-bit register, except bit 12, go to IF2. Depending on the state of bits 14 and 15, both the D/A and I/O drivers can be controlled by the same 16 bits.

For dislodging the drop, a pulse from the computer is applied to the drop-dislodge solenoid, which then hits the clamp that holds the HMDE.

With bit 14 high, and bit 15 low, bits 0—10 control the output current of the D/A. This output is connected to the input of the 174A summing amplifier which controls the initial potential applied to the cell. The D/A provides 1 μA/bit. Adding 1 bit decreases the current by 1 μA. When bits 0—10 are all set to 1, the output current to the summing amplifier will be 0 μA, and the potential applied to the cell will be 0 V. Each bit added will increase the potential 10 mV until at 100 μA the applied potential is —1.0 V. When bit 15 is high (1) and bit 14 is low (0), bits 0—4 and bit 12 set the I/O drivers high or low; these, in turn, control the various relays.

Software. All software was written in FORTRAN V. The programs allow the user to select purge time, initial potential, final potential, current range, deposition time, and equilibration time. The values for the applied deposition potential $E_{(\mathrm{app})}$ are selected from E(initial) to E(initial) + (0.3 V) from a set of originally randomized potentials. A normal a.s.v. experiment is run at a selected potential and the data are then stored in the first file. Each subsequent set of data is stored in a new file. The program selects 30 potentials, 0.01 V apart, in covering the 0.3-V range chosen. While the program is running, the status of the 174A is displayed by the "S" register on the HP21MX front panel.

Reagents

All solutions were prepared with deionized water. Standard stock solutions of cadmium(II) were prepared from cadmium nitrate. Unless otherwise indicated, all chemicals used were analytical-reagent grade. All sea water used was collected from Scripps Pier, San Diego, California, and filtered through a 0.22-μm Millipore system.

The mercury used for filling the capillary was reagent-grade and was triple distilled; it was further cleaned by washing with nitric acid and then passing through a pinhole made in a filter paper.

The nitrogen gas used was ultra-pure (99.95%) (Airco Co.) passed once through a Messer Griesheim Oxisorb filter (Parco).

Procedures

For each experiment the cell was washed with 8 M nitric acid and then rinsed several times with quartz-distilled water. The cell was filled with 25 ml of quartz-distilled water and the appropriate reagents added. The experiment was then placed under computer control after the operator had entered the necessary experimental and instrument parameters. The following steps were carried out under the program control: (1) the solution was purged with nitrogen gas for 30 s (15 min for the first run); (2) the old drop was dislodged and a new drop formed; (3) the specified deposition potential was applied for the specified time; (4) the stirrer was turned off, and the solution allowed to equilibrate for 15—30 s; (5) the applied potential was decreased by 5 mV s^{-1}, starting at the deposition potential; (6) while the potential was decreasing, the A/D converter sampled the x-axis (E_{app}) and y-axis (I) outputs at 500-ms intervals. These (E_{app}, I) data points were stored in a data file.

After the scan, the experiment was either terminated or a new deposition potential was selected by the program and the procedure repeated. A typical computer plot for stripping polarography is shown in Fig. 4.

To verify the relationship indicated by eqn. (15), solutions of 10^{-5}—10^{-8} M cadmium(II) which contained 10^{-1}—10^{-4} M ethylenediamine in 0.1 M KNO_3 were studied.

RESULTS AND DISCUSSION

Addition of 10^{-2} M ethylenediamine (en) to a solution containing 10^{-8} M cadmium(II) in 0.1 M KNO_3 caused a shift of the half-wave potential of —168 mV ± 2 mV (Fig. 5). The value for $\Delta E^*_{1/2}$, calculated from eqn. (15) is —166 mV. The slope of the reduction wave was 27 mV ± 1 mV, indicating the reversibility of this system and thus allowing application of eqn. (15). This same equation can also be used to determine the formula of the complex by solving for P, which may be determined from the variation of $E^*_{1/2c}$ with C_x. A simple analytical expression is obtained by differentiation of eqn. (15) to give:

$$d(E^*_{1/2c})/d(\log C_x) = -0.0592\,P/n \qquad (16)$$

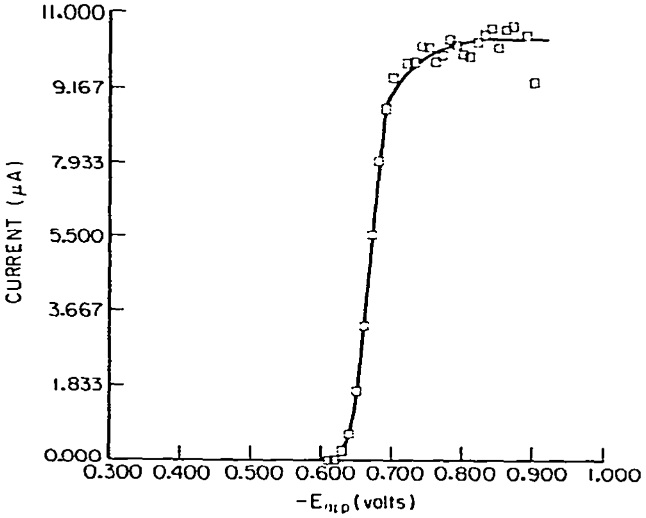


Fig. 4. Computer-generated plot of 10^{-5} M cadmium(II) in 0.1 M KNO_3.

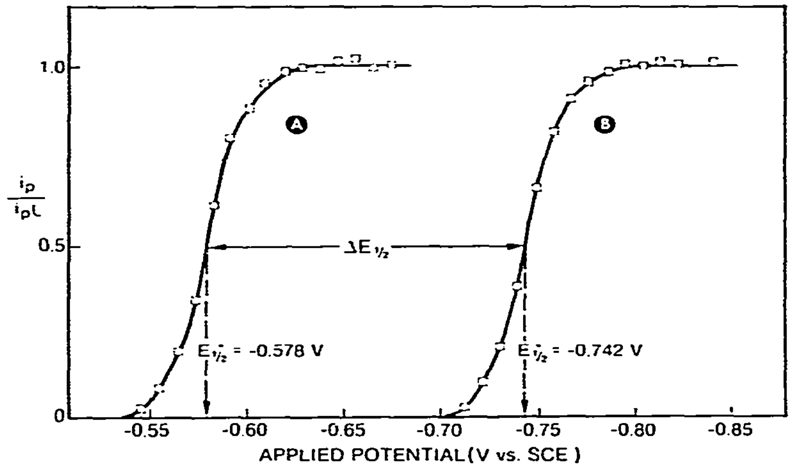


Fig. 5. Shift of the half-wave potential on addition of 10^{-2} M ethylenediamine to 10^{-8} M cadmium(II) in 0.1 M KNO_3. (A) 10^{-8} M cadmium(II); (B) 10^{-8} M cadmium(II) + 10^{-2} M ethylenediamine.

where $E^*_{1/2s}$ and f_x in eqn. (15) are assumed to be constants as C_x is varied; x is also assumed to be non-ionic in this case. Subject to these assumptions, the value of P can be obtained directly from the slope of the plot (solid line) shown in Fig. 7. With ethylenediamine concentrations of 10^{-1}—10^{-4} M, the experimental value of the slope $d(E^*_{1/2c})/d(\log [en])$ is —0.087 V ± 0.001 V. Since $n = 2$ for the reduction of the cadmium(II) complex, $P = 2.89$. This indicates that under the given conditions, the predominating complex is $Cd(en)_3^{2+}$.

To find the dissociation constant of the $Cd(en)_3^{2+}$ complex, eqn. (15) was used. Substituting —0.578 V for $E^*_{1/2s}$, —0.742 for $E^*_{1/2c}$, 1×10^{-2} M for C_x, and $P = 3$, the value obtained was $K_c = 2.48 \times 10^{-12}$, which within experimental error, is in good agreement with a literature value of $K_c = 2.32 \times 10^{-12}$ [23].

Application to sea water

Addition of 10^{-1}—10^{-3} M ethylenediamine to sea water containing 10^{-8} M Cd(II) caused a shift of the half-wave potential of —126 mV ± 2 mV (see Fig. 6). This shift is less than that observed for $Cd(en)_3^{2+}$ in 0.1 M KNO_3 and reflects the competitive complexation of cadmium by chloride ions. The slope of the stripping polarographic reduction wave for Cd(II) in sea water was found to be 29 mV ± 1 mV for all concentrations of ethylenediamine and cadmium used. This indicates that the reduction/oxidation reaction $Cd^{2+} \rightleftharpoons Cd(Hg)$ in sea water is reversible and allows the application of eqns. (1) and (15) for investigative purposes.

The complexation of cadmium(II) in sea water was further studied by observing the effect of successive additions of ethylenediamine on $E^*_{1/2}$ values (Fig. 7). It can be predicted from eqn. (15) that no change in $E^*_{1/2}$ will be ob-

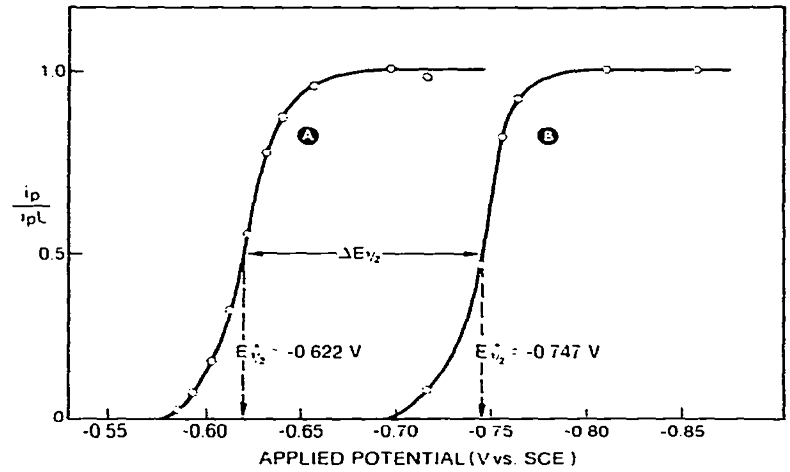


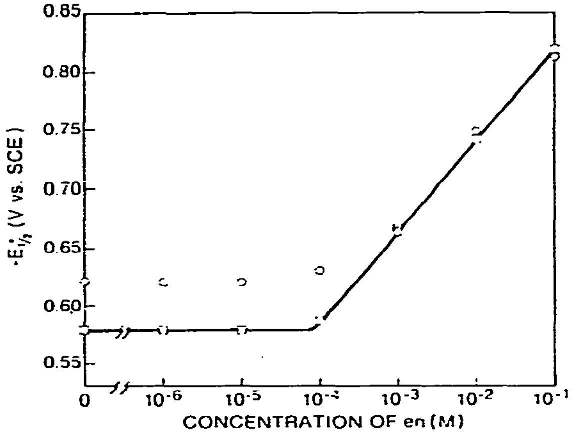
Fig. 6. Shift of the half-wave potential on addition of 10^{-2} M ethylenediamine to 1×10^{-8} M cadmium(II) in sea water. (A) and (B) as in Fig. 5.

served until $(C_x f_x)^p \leqslant K_c$. For $Cd(en)_3^{2+}$ ($K_c = 2.3 \times 10^{-12}$), the slope $d(E^*_{1/2})/d(\log [en])$ would be expected to be 0 mV up to a concentration of ca. 10^{-4} M ethylenediamine; at values above 10^{-4} M, the slope should be equal to 87 mV. As can be seen in Fig. 7, the theoretical and experimental points are practically identical for the KNO_3 solution. The second curve in Fig. 7 describes the behavior of $E^*_{1/2}$ for Cd(II) in sea water. In contrast to the KNO_3 system, the curve for sea water shows a gradual change of $E^*_{1/2}$ between 10^{-5} and 10^{-3} M ethylenediamine. This change can be explained by the competitive complexation of Cd(II) by chloride and ethylenediamine.

Figure 8 shows the calculated distribution of Cd(II) in 0.1 M KNO_3 and in sea water at various concentrations of ethylenediamine. The data were obtained by use of a modified version of a computer program which calculates the equilibrium concentration distribution of chemical species in aqueous systems [24]. In a 0.1 M KNO_3 solution, cadmium(II) is approximately 98% complexed with 10^{-4} M ethylenediamine. In model sea water (0.55 M Cl^-, 0.45 M Na^+; 0.052 M Mg(II); 0.01 M Ca(II); 0.0097 M K^+; 0.0012 M CO_3^{2-}; 0.028 M SO_4^{2-}; pH 8.0) the cadmium(II) is initially 95% complexed as $CdCl_2$. As ethylenediamine is added, the chloride is slowly replaced. However, the Cd(II) is not significantly (ca. 98%) complexed by ethylenediamine until ca. 10^{-3} M has been added.

The agreement between the calculated and experimental results indicates the usefulness of stripping polarography for studying and verifying at realistic concentrations, model systems of trace metals in natural media.

In conclusion, computer-assisted stripping polarography offers a means of applying classical polarographic methods to the study of ligand complexation of trace metals at sub-10^{-8} M levels. These initial investigations of cadmium—ethylenediamine complexes in sea water indicate the feasibility of using this



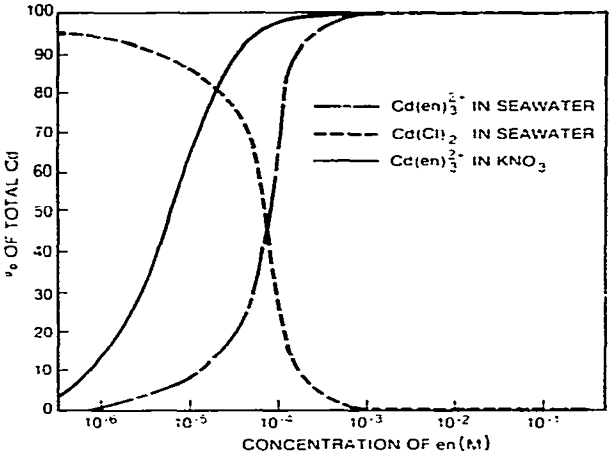


Fig. 7. Effect of ethylenediamine concentration on the half-wave potential for 10^{-8} M cadmium(II) in sea water (○) and 0.1 M KNO_3 (□). The line represents the theoretical plot for 0.1 M KNO_3.

Fig. 8. The calculated distribution of cadmium(II) in 0.1 M KNO_3 and in sea water at various concentrations of ethylenediamine.

method for further characterization studies of other trace metals, such as lead, zinc, and copper, at sub-10^{-8} M levels.

The use of the mini-computer was found to be essential because of the amount of data and time required for stripping polarographic curve generation.

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