

THE NEUTRAL OXYGEN DONOR IN COMPLEXES OF LEAD AND CADMIUM: A DIFFERENTIAL PULSE POLAROGRAPHIC, POTENTIOMETRIC AND CALORIMETRIC STUDY

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Abstract—Differential pulse polarography has been used to determine the formation constants of Pb^{II} with ethylenediamine (en) at ionic strength 0.1 M and at 5, 25 and 50°C. The equilibria between Pb^{2+} and the ligands en and OH^- are established rapidly on the polarographic time scale for all complexes studied, so that one peak is observed, that for the metal ion and its labile complexes. At 5°C the following complexes were found: $\text{M}(\text{HL})$, ML , ML_2 and $\text{ML}_2(\text{OH})$, for which the stability constants ($\log \beta$) were found to be 12.97, 5.62, 9.70 and 13.45, respectively. At 25 and 50°C, the complexes ML , ML_2 , $\text{ML}_2(\text{OH})$ and $\text{ML}_2(\text{OH})_2$ were found and their stability constants were found to be 5.05 and 4.43, 8.67 and 7.37, 12.6 and 11.75, 15.29 and 14.8, respectively. The Lingane equation was modified to allow calculation of formation constants for labile complexes of lead with the two ligands, en and OH^- . The two stepwise protonation constants of en at an ionic strength of 0.1 M and temperatures of 5 and 50°C are reported and their values were found to be $\log K_1 = 10.44$ and 8.98 and $\log K_2 = 7.39$ and 6.53, respectively. From the polarographic data, thermodynamic quantities were derived for the overall complex formation reactions of Pb^{II} with en and the values of ΔH° (kJ mol^{-1}) for ML , ML_2 , $\text{ML}_2(\text{OH})$ and $\text{ML}_2(\text{OH})_2$ were found to be -44.7 , -90.6 , -65.7 and -39.1 , respectively. The stepwise protonation constants of N,N,N',N' -tetrakis(2-hydroxypropyl)ethylenediamine (THPED) at an ionic strength of 0.5 M and 25°C are reported and their values ($\log K$) were found to be 8.85 and 4.38. At 25°C and an ionic strength of 0.5 M, the complexes ML , $\text{M}(\text{HL})$ and $\text{ML}(\text{OH})$ of Cd^{II} and Pb^{II} with THPED were found and their cumulative stability constants ($\log \beta$) were found to be 7.98 and 7.51, 11.75 and 11.3, 11.14 and 13.00, respectively. The values of ΔH° (kJ mol^{-1}) for ML complexes of Cd^{II} and Pb^{II} with THPED were found to be -48.0 . Values of ΔG° , ΔH° and ΔS° for the ligand displacement reaction in which en is displaced by THPED in ML complexes of Pb^{II} and Cd^{II} are also reported and discussed. It is suggested that the coordination numbers of Pb^{II} in the complexes $\text{Pb}(\text{en})_2^{2+}$ and $\text{Pb}(\text{THPED})_2^{2+}$ in solution probably differ.

Ligand design has become an important area of research in coordination chemistry because of the use of specially designed metal complexes in biomedical applications such as radiography,¹ positron emission tomography,² magnetic resonance imag-

ing³ and cancer therapy,⁴ to mention but a few examples. Among the molecular structural features that are available to the ligand designer for incorporation into ligands for the purpose of achieving desired complex stability and metal ion selectivity are the nature of the ligand donor atoms and the size of chelating ring systems.

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The neutral oxygen donor is of considerable

importance,⁵ since it is the donor atom of the most important solvent, water, and is also present in ligands such as crown ethers⁶ and cryptands,⁷ as well as naturally occurring ligands such as monensin and nonactin.⁸ An important aspect of the neutral oxygen donor⁹ is that its presence in a ligand leads to enhanced selectivity for large relative to small metal ions. This is undoubtedly the basis⁸ of its presence in biological ligands whose function is selectively to complex large¹⁰ metal ions such as sodium, potassium and calcium.

An example of the selectivity pattern produced by the neutral oxygen donor is seen in Fig. 1, where the change in the complex stability, $\Delta \log K$, produced on adding 2-hydroxypropyl arms on ethylenediamine (en) to give *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (THPED) shows a strong correlation with metal ion radius.¹⁰ Also shown in Fig. 1 is $\Delta \log K$ for en and 1,10-diaza-4,7,13,16-tetraoxocyclooctadecane (18-aneN₂O₄), showing that the effect of the neutral oxygen donor on selectivity is similar whether the neutral oxygen donor is part of an open-chain ligand such as THPED or of a macrocycle such as 18-aneN₂O₄.

A point of interest here is the origin of the selectivity for large metal ions produced by the presence of the neutral oxygen donor. Two factors are important here.⁵ The first is the basicity of the oxygen donors, which increases in the gas phase¹¹ in the order $H_2O < ROH < R_2O$ ($R = \text{alkyl group}$). Thus, the alcoholic oxygens of THPED are expected to be stronger donors than water itself, while the ethereal oxygen donors of a macrocycle such as 18-aneN₂O₄ are still stronger donors. One has then to account for why only large metal ions form more stable complexes in the presence of neutral oxygen donors. A steric factor,⁵ namely the size of the chelate ring,¹² appears to be involved. Below are shown the ideal geometries for a five-membered chelate ring and a six-membered chelate ring containing neutral oxygen donors, represented respectively by ethyleneglycol (EG) and 1,3-dihydroxypropane (DHP).

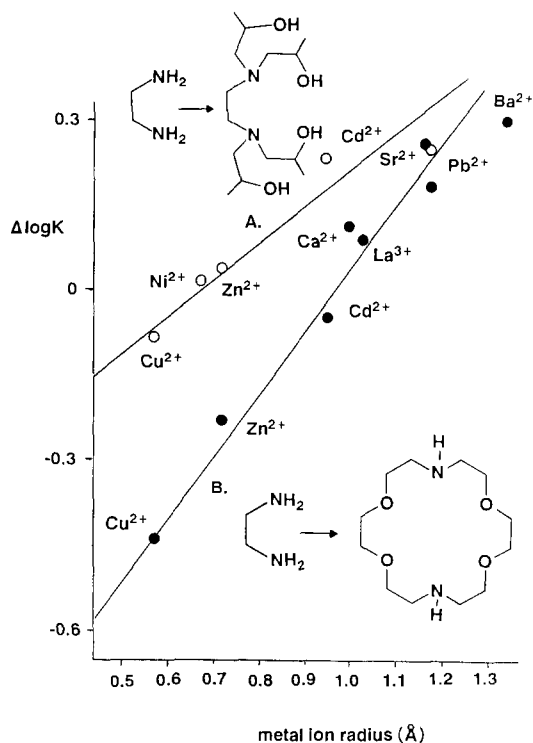
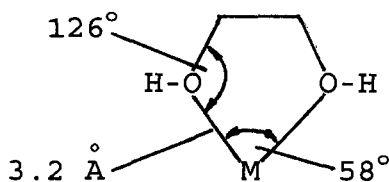
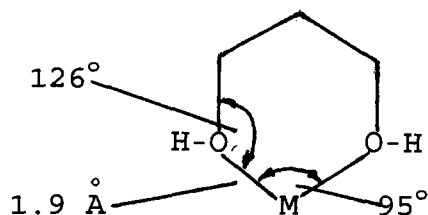


Fig. 1. Correlations between the change in complex stability constant, $\Delta \log K$, produced on addition of four 2-hydroxypropyl arms on en to give THPED (○), conversion of en to 18-aneN₂O₄ (●), and metal ion radius.

A major difference in the preferred geometry for chelate rings containing saturated nitrogen donors, on the one hand, and oxygen donors on the other arises from the tetrahedral geometry around a saturated nitrogen donor coordinated to a metal ion, and the near trigonal planar geometry¹³ around a coordinated oxygen donor. Neutral oxygen donors are almost invariably part of five-membered chelate ring systems, and it is seen below that such a ring system coordinates large metal ions with low strain energy. The M—O bond length of 3.2 Å that leads to minimum strain in the chelate ring corresponds to the longest M—O bond lengths known, which would correspond to the largest¹⁰ metal ions such



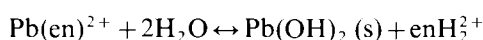
five membered chelate ring



six membered chelate ring

as Cs^+ . Inclusion of a small metal ion in a five-membered chelate ring containing neutral oxygen donors would lead to a high strain energy, and hence to low complex stability. On the other hand, saturated nitrogen donors prefer shorter M—L bond lengths. Both of these proposals about the origin of the selectivity for large metal ions engendered by neutral oxygen donors require that the added stability be an enthalpy effect. Strain energy effects, as well as the increased basicity of alcoholic or ethereal oxygens as compared with the water molecules that they displace on complex formation, should lead to complexes that are enthalpy stabilized relative to the analogues without the alcoholic groups. Accordingly, we set out to measure enthalpies of complex formation of the large metal ions Cd^{II} and Pb^{II} with en and THPED. Where possible, measurements of enthalpy changes for metal–ligand complex formation reactions in this study were carried out by direct titration calorimetry, supplemented, where required, by potentiometric determination of formation constants.

The Pb–en system, however, presents difficulties for both potentiometric and calorimetric studies. A value of $\log K_1 = 5.04$ (at 25°C and an ionic strength of 0.1 M) for the $\text{Pb}(\text{en})_2^{2+}$ complex has been reported¹⁴ from a glass electrode potentiometric study, the details of which highlight some of the difficulties involved in studying complexes of Pb^{II} with amines. In order to prevent hydrolysis of the metal ion and precipitation of the solid hydroxide, $\text{Pb}(\text{OH})_2$ (s), the potentiometric study was carried out in 0.1 M ethylenediammonium nitrate to keep the position of the equilibrium



as far as possible to the left. The potentiometric study¹⁴ was somewhat unsatisfactory in that it did not allow for a very high extent of complex formation before precipitation of lead hydroxide occurred. Furthermore, under these conditions, none of the higher complex species, such as $\text{Pb}(\text{en})_2^{2+}$, were detected before onset of precipitation. Similarly, it was found in the present work that the Pb–en system could not be studied calorimetrically because precipitation of the metal hydroxide occurs under experimental conditions appropriate to calorimetric measurements.

As an alternative approach, we report here a study of the Pb–en system by differential pulse polarography (DPP). Speciation studies by polarography typically require low concentrations of metal ion (10^{-4} – 10^{-5} M) and high ligand-to-metal ratios of up to 1000. Several systems have already been studied by the present authors using this tech-

nique.^{15–17} In this study, we report formation constants for species formed in the Pb–en system at three temperatures, 5, 25 and 50°C , from which, by means of the van't Hoff equation, values for the corresponding enthalpy changes are determined. The approach to the interpretation of the polarographic data and calculation of formation constants for labile complexes of lead is described. Four new complexes of lead with en, together with thermodynamic quantities for the corresponding complex formation reactions, are reported.

A further reason for our interest in complexes of Pb^{II} with ligands containing neutral nitrogen and oxygen donors is the observation^{15,16} that there is considerable similarity between the chemistry of Pb^{II} and of the isoelectronic ion Bi^{III} . The coordination chemistry of the Bi^{III} ion has been the subject of much interest recently. It has, for example, been predicted^{18–20} that Bi^{III} should have a great affinity for nitrogen donor ligands, and this has been confirmed experimentally by polarography^{15,16} for chelating open-chain and macrocyclic ligands. Crystals of $\text{Bi}^{\text{III}}-(12\text{-aneN}_4)-(10\text{-C}_4\text{O}_4)_3$ have been grown and their crystallographic structure solved.²¹ A good correlation between $\log K_1$ values for Pb^{II} and Bi^{III} has been demonstrated,¹⁶ which is helpful in solving problems associated with Bi^{III} chemistry.

EXPERIMENTAL

Instrumentation

Polarography. Differential pulse polarograms were obtained with the use of a Metrohm 506 Polarecord and a Model 663 VA stand. A multi-mode electrode (Metrohm, cat. no. 6.1246.020) was employed as the working electrode and used in the dropping mercury electrode mode with a drop time of 1 s. A saturated calomel electrode and a platinum electrode (both Metrohm) were used as reference and auxiliary electrodes, respectively. A pulse height of 50 mV and step height of 4 mV were used. The pH of the solutions was measured to within 0.002 pH units with the use of a PHI 72 pH meter and combination glass electrode cat. no. 39536 (both Beckman). The temperature of the cell was controlled to $\pm 0.1^\circ\text{C}$. High purity nitrogen was used for deaeration of the sample solutions.

Potentiometry. The potentiometric titrations were performed in a Metrohm jacketed glass reaction vessel, equipped with a magnetic stirrer, and thermostatted at 25.0°C by water circulating from a constant temperature bath. The e.m.f. of the cell was measured to ± 0.1 mV with a Radiometer PHM 84 Research pH meter equipped with a Radiometer MQ 1069 combination glass electrode. A stream of

high purity nitrogen was bubbled through the test solution during the entire duration of the experiment for the measurements involving the THPED ligand. For measurements involving the more volatile en, the stream of nitrogen was stopped once ligand was introduced into the vessel. Grade "A" volumetric glassware was used.

Calorimetry. Enthalpy changes were measured by means of a precision titration calorimeter. The construction and testing of the calorimeter have been described previously.²² The titration calorimeter consists essentially of an LKB 8721-2 titration calorimetry assembly with an electronic control system designed and constructed by MINTEK. Since the report on the construction of the calorimeter was published, some changes have been made to the electronic assembly.²³

Materials

The ligands ethylenediamine and *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (Aldrich Chemie, 98%) were obtained from Aldrich and used as received. All other reagents used were of analytical grade. Pure water for the use in polarographic studies was obtained by passing deionized water through a Milli-Q-water purification system. Other solutions were made up in distilled and doubly-deionized water. Solutions of THPED were prepared weekly and standardized by potentiometric titration against nitric acid, which had itself been standardized against freshly recrystallized borax (BDH Analar).²⁴ Concentrations of cadmium and lead were refined by simultaneous variation with formation constants using the ESTA program.

Procedure

Polarography. In a typical run, the polarographic cell contained Pb^{II} (10^{-5} M) in 0.1 M HNO_3 . Three different ligand:metal ratios were used (in the range 750–1000) to aid in establishing the correct species model and were prepared by addition of the appropriate amount of a 0.1 M standard solution of the ligand to the vessel containing metal ion solution. After recording a polarogram, the pH of the solution was adjusted upwards in steps of about 0.050–0.200 pH units, by addition of NaOH solution from a microburette graduated to 0.01 cm^3 , and a new polarogram recorded. In this way a set of between 40 and 60 polarograms of the species present in the solution was obtained as a function of pH. Polarograms of the ligand alone as a function of pH were also run in a similar way to identify ligand peaks on the polarogram. Equilibration of

the metal–ligand solutions occurred within a few minutes. Polarograms were recorded on solutions adjusted to an ionic strength of 0.1 M. High purity nitrogen, which was used to remove air from the polarographic cell, was presaturated with en to avoid ligand loss by volatilization.

Potentiometry. To establish the protonation constants of en in a solution of ionic strength 0.1 M at different temperatures, potentiometric titrations were performed at 5 and 50°C. The first titration involved addition of 0.01 M HNO_3 in 0.09 M NaNO_3 to the cell containing 0.01 M NaOH and 0.09 M NaNO_3 , from which the E° and response slope of the glass electrode were calculated. Next, a ligand solution containing 1.01×10^{-2} M en in 0.1 M NaNO_3 was titrated with 1.005×10^{-2} M HNO_3 and 0.09 M NaNO_3 . The potential of the cell was measured to within ± 0.1 mV for each addition of the titrant. The nitrogen stream was purified by passage through 10% NaOH, 10% H_2SO_4 and 0.1 M NaNO_3 solutions before entering the titration cell during cell calibration. To establish formation constants for complex formation of Cd^{II} and Pb^{II} with THPED, the potentiometric cell was calibrated by a method similar to that outlined above. Solutions containing known concentrations of the THPED ligand (0.005–0.01 M) and metal ion (0.004–0.008 M) were then titrated with an acid solution (0.01 M) to strip the ligand from the metal ion. All solutions used in the THPED measurements were made up to an ionic strength of 0.5 M using NaNO_3 .

Calorimetry. Solutions containing known concentrations of metal ions (0.01 M) were titrated continuously with a solution of THPED (0.2 M) at a fixed rate. All solutions were made up to an ionic strength of 0.5 M using NaNO_3 as background electrolyte. The temperature of the reaction vessel was recorded as a function of titrant added.

Treatment of polarographic data

A computer program ML-SPEC was written for the IBM PC that allows for the calculation of formation constants from polarographic data. It consists of three parts. One is dedicated to systems where non-labile complexes are formed on the polarographic time scale. The way it calculates a formation constant for a metal complex thought to be formed in a solution over a pH region where two polarographic peaks are observed, that of metal ion and of an unknown complex of the metal, has been described elsewhere.¹⁷

The second part of the program calculates formation constants for complexes which are labile on the polarographic time scale. To treat a system in

which more than one ligand is coordinated to a central metal ion and where there is a region of pH in which one complex is the predominant species present in the solution, the Lingane²⁵ equation was used in a modified form. For the present work, in which en and the hydroxide ion are considered as ligands, the equilibrium may be written as



and the Lingane expression can be readily expanded to

$$\Delta E_{\text{peak}} - \frac{RT}{nF} \ln \left(\frac{i_c}{i_s} \right) = \frac{RT}{nF} \ln \beta_{ML_j(OH)_b} + j \frac{RT}{nF} \ln [L] + b \frac{RT}{nF} \ln [OH]. \quad (2)$$

In this equation, M represents the metal ion, L represents a ligand (in our case en), and the brackets denote molar concentrations as the experiment is to be performed at constant ionic strength (charges on ions are omitted for simplicity). ΔE_{peak} is the difference in the DPP peak potentials between the simple metal ion and the complexed ion. RT/nF has the usual meaning and i_s and i_c represent the peak currents for the simple and complexed metal ion, respectively. When protonated complexes are formed, [OH] in (1) and (2) is replaced by [H] and eq. (2) holds, provided that the particular protonated complex is a predominant species in the solution for the particular pH region considered. When complexes of the form ML_j are being considered, then parameter b is set to zero and eq. (2) simplifies to the usual form of the Lingane equation. The modification of the Lingane equation used here is similar to that used by Fisher and Hall,²⁶ who extended the equation developed by DeFord and Hume.²⁷ This part of the ML-SPEC program can also graphically present plots of the shift in the polarographic peak potential (half-wave potential), first as a function of calculated free ligand concentration and second as a function of the observed pH of the samples. These two plots are of great help in the interpretation of electrochemical processes occurring at the mercury electrode and are used to infer the nature of the species present in solution.

The third part of the ML-SPEC program calculates and presents, in graphical form, the predicted species distribution as a function of pH, taking into account all the species incorporated in the model, including those species which are known to be present (with fixed formation constants), and others for which formation constants have been calculated. This graph is compared with recorded

polarograms and is used to test models of species proposed and their calculated formation constants.

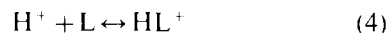
RESULTS AND DISCUSSION

Potentiometric studies

Protonation of en and THPED. The protonation of en was studied by glass electrode potentiometry carried out using a cell containing a glass-indicating electrode calibrated for measurement of hydrogen ion concentration (see Experimental). A solution of en, which was initially slightly alkaline and made up in a background of 0.1 M NaNO₃ ($L_T = 1.03 \times 10^{-2}$ M; $OH_T = 7.413 \times 10^{-4}$ M at 5°C and $OH_T = 6.026 \times 10^{-4}$ M at 50°C), was titrated with nitric acid, also made up in a background of NaNO₃ ($H_T = 1.0049 \times 10^{-2}$ M; $Na_T = 0.490$ M). Values of the protonation function, \bar{Z}_H ,²⁸ defined as

$$\bar{Z}_H = \frac{H_T - [H] + [OH]}{L_T} \quad (3)$$

were calculated for each datum point and are plotted (\times for 5°C and \circ for 50°C) vs observed values of $pH = -\log_{10}[H]$ in Fig. 2. The protonation function can be interpreted as the average number of protons coordinated per ligand molecule. It is clear that the ligand accepts two protons in a stepwise fashion and is virtually completely protonated at pH values below about 6.6 and 5.3, and is completely deprotonated at pH values above about 11.6 and 10.1 at 5 and 50°C, respectively. The program ESTA²⁹ was used to calculate the protonation constants of en. The values of the protonation constants corresponding to the reactions



at an ionic strength of 0.1 M and at 5 and 50°C found in this work, together with the literature values¹⁴ reported for 25°C, are presented in Table 1.

Theoretical protonation curves, calculated on the basis of reactions (4) and (5), are shown as continuous curves in Fig. 2. These curves comprise values of the protonation function \bar{Z}_H calculated using the stability constants given in Table 1 and are plotted vs calculated pH. The good agreement between the observed and calculated formation functions indicates that the proposed model gives a satisfactory account of the potentiometric data.

Solutions of the ligand THPED (0.01–0.15 M) were made up in a background of 0.5 M NaNO₃ and were titrated with nitric acid (0.01–0.24 M),

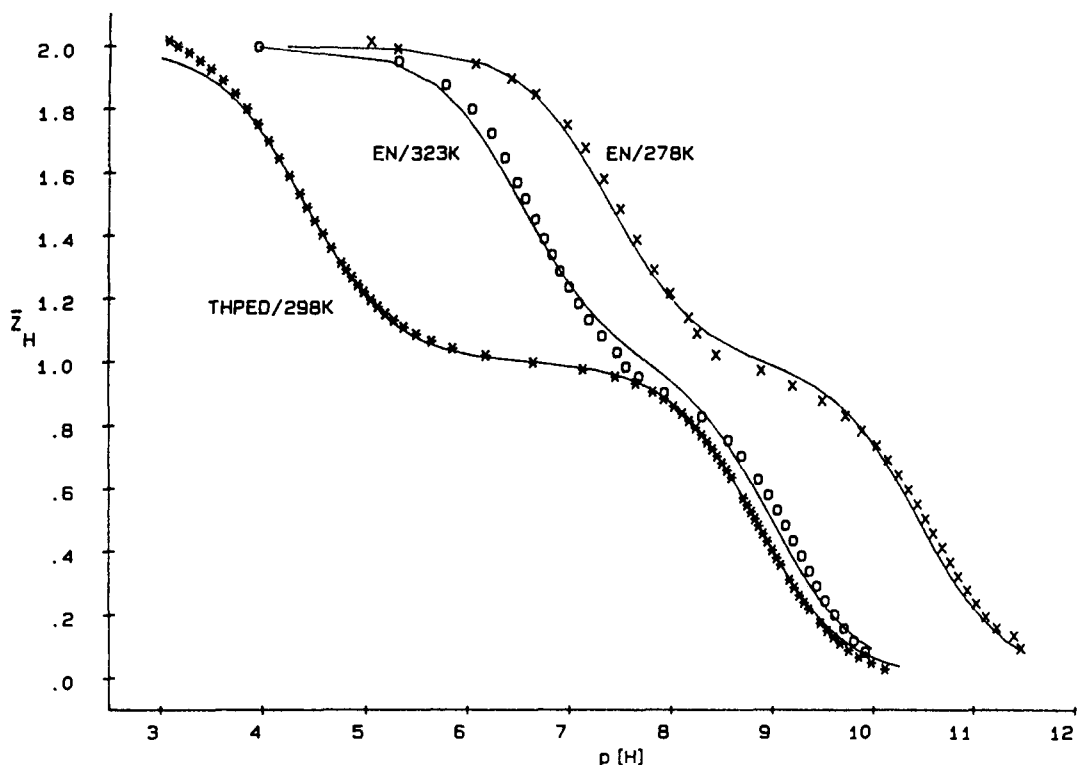


Fig. 2. Experimental and theoretical (—) protonation curves for the protonation of en (○, ×) and THPED (*) in a background of 0.1 M and 0.5 M NaNO₃, respectively. \bar{Z}_H is the protonation function described in the text.

Table 1. Protonation constants for the ligands en and THPED, and formation constants for complex formation of Cd^{II} and Pb^{II} with THPED, determined by glass electrode potentiometry in this work and elsewhere

L	Temp. (°C)	Equilibrium	Log β	Ref.
en	5	L + H ⁺ ⇌ HL ⁺	10.44 ^a ± 0.02	this work
		HL ⁺ + H ⁺ ⇌ H ₂ L ²⁺	7.39 ^a ± 0.03	this work
en	25	L + H ⁺ ⇌ HL ⁺	9.89	4
		HL ⁺ + H ⁺ ⇌ H ₂ L ²⁺	7.08	4
en	50	L + H ⁺ ⇌ HL ⁺	8.98 ^a ± 0.01	this work
		HL ⁺ + H ⁺ ⇌ H ₂ L ²⁺	6.53 ^a ± 0.02	this work
THPED	25	L + H ⁺ ⇌ HL ⁺	4.41 ± 0.03	this work
		HL ⁺ + H ⁺ ⇌ H ₂ L ²⁺	4.41 ± 0.03	this work
THPED	25	Cd ²⁺ + L ⇌ CdL ²⁺	7.98 ± 0.02	this work
		Cd ²⁺ + L + H ⁺ ⇌ Cd(HL) ³⁺	11.75 ± 0.03	this work
		Cd ²⁺ + L + OH ⁻ ⇌ CdL(OH) ⁺	11.14 ± 0.02	this work
THPED	25	Pb ²⁺ + L ⇌ PbL ²⁺	7.51 ± 0.02	this work
		Pb ²⁺ + L + H ⁺ ⇌ Pb(HL) ³⁺	11.3 ± 0.1	this work
		Pb ²⁺ + L + OH ⁻ ⇌ PbL(OH) ⁺	13.00 ± 0.03	this work

Unless otherwise indicated, determinations were carried out at an ionic strength of 0.5 M.
^aIonic strength 0.1 M.

also made up in a background, of 0.5 M NaNO₃. The temperature was controlled to 25 ± 0.01°C. Solutions of ligand were standardized by potentiometric titration against standard acid using sim-

ultaneous ESTA refinement of ligand concentration and the protonation constants. Protonation constants are presented in Table 1. Typical experimental data obtained in the titrations are shown

as asterisks in Fig. 2, in the form of a plot of \bar{Z}_H vs pH. Good agreement was obtained between observed and calculated values of the protonation function. The values obtained compare well with those reported in the literature.

Complex formation of Cd^{II} and Pb^{II} with THPED. Potentiometric titrations were carried out as outlined above (see Experimental). Values of the complex formation function, \bar{Z}_M ,²⁸ defined by

$$\bar{Z}_M = \frac{L_T - A \left(1 + \sum_{n=1}^N \beta_{n01} [H^+]^n \right)}{M_T}, \quad (6)$$

where

$$A = \frac{H_T - [H^+] + [OH^-]}{\sum_{n=1}^N \beta_{n01} [H^+]^n}, \quad (7)$$

were calculated for each datum point and typical complex formation curves, i.e. plots of \bar{Z}_M vs values of $pA = -\log_{10} A$ (○ for cadmium and * for lead) are shown in Fig. 3. Under circumstances in which H^+ and OH^- are not directly involved in any metal-containing species in solution, the complex formation function can be interpreted as the average

number of ligand molecules bound to a metal ion, and the quantity A as the concentration of free (uncomplexed and unprotonated) ligand in solution.

For both systems a "back-fanning" feature was evident in the formation curves at lower values of pA , a feature that is fairly typical for systems in which complex hydrolysis takes place.

Formation constants determined in this work are given in Table 1. The good agreement obtained between observed and calculated formation functions indicates that the proposed models of the species formed in solution, and corresponding formation constants, give a satisfactory account of the potentiometric data.

Polarographic studies

In Fig. 4, a plot of species distribution (expressed as a fraction of a total lead concentration) vs pH at 25°C and at an ionic strength of 0.1 M is presented for a ligand-to-metal ratio of 1.5 and a total lead concentration of 1×10^{-3} M, fairly typical conditions for glass electrode potentiometry.

The Davies equation was used to estimate formation constants for $Pb(OH)_i$ species at an ionic

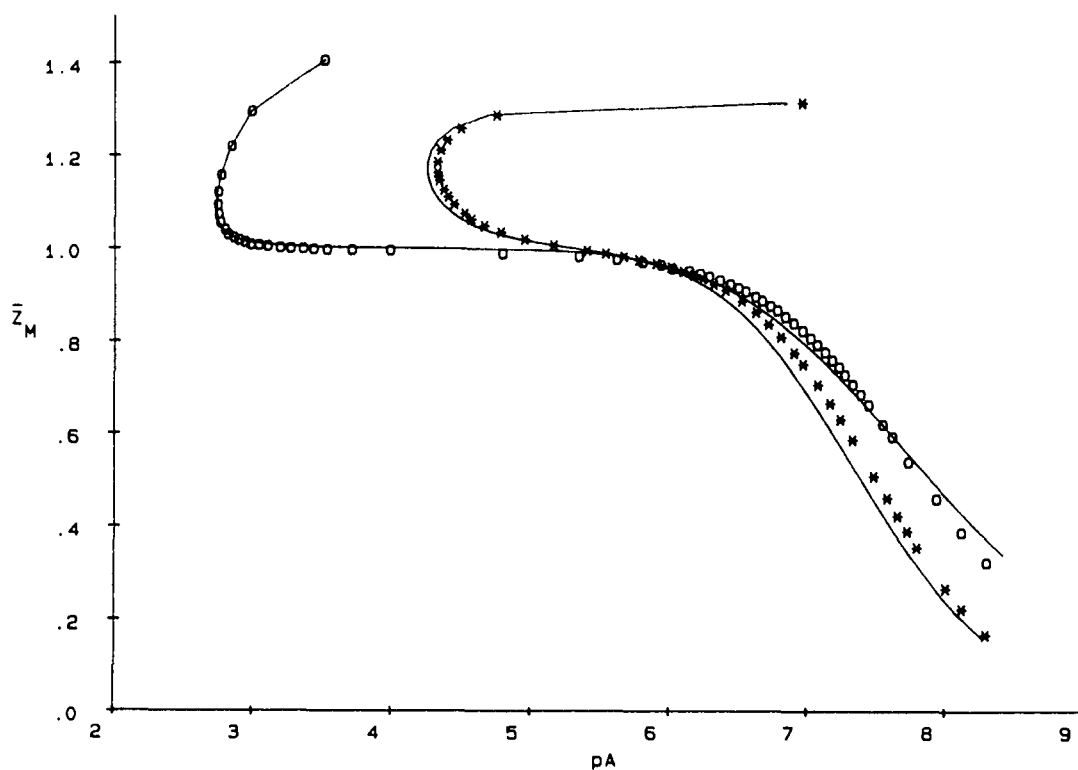


Fig. 3. Experimental and theoretical (—) complex formation curves for cadmium (○) and lead (*) with THPED in a background of 0.5 M $NaNO_3$. $pA = -\log_{10} A$, where the quantity A and the complex formation function \bar{Z}_M are described in the text.

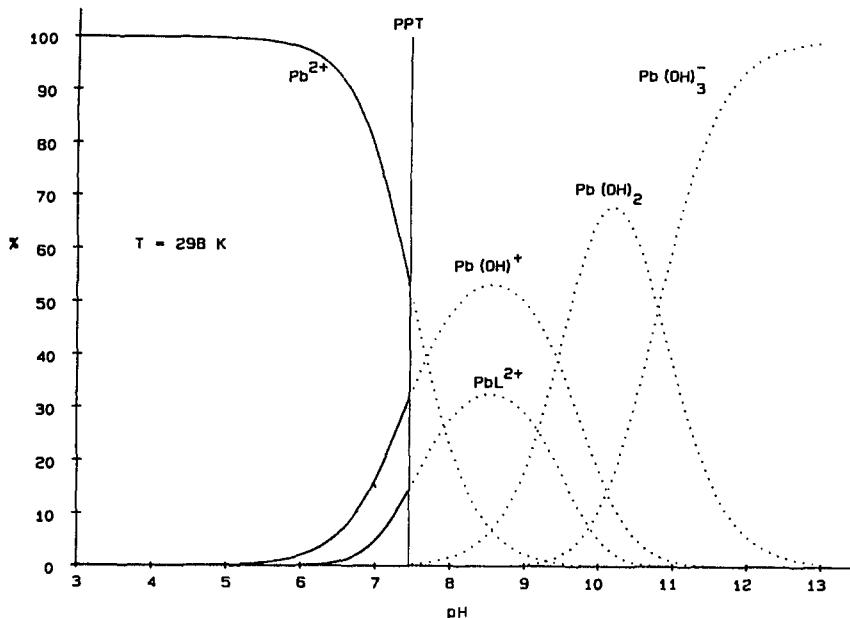


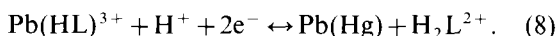
Fig. 4. Species distribution, expressed as a fraction of total lead concentration, as a function of pH, at 25°C, and at an ionic strength of 0.1 M, $M_T = 1 \times 10^{-3}$ M, and a ligand-to-metal ratio of 1.5. Dotted lines represent theoretical concentrations of lead species calculated ignoring precipitation that takes place at a pH value indicated by the solid vertical line labelled PPT.

strength of 0.1 M, since in the literature values for these species are available at an ionic strength of 0.3 M only. Dotted lines represent theoretical concentrations of species, because in practice precipitation takes place at a pH value of about 7.4 (solid vertical line labelled PPT) before very much of the Pb-en complex is formed. This graph illustrates why potentiometry is not a suitable technique for study of the Pb-en system, and we found it difficult to obtain a reliable value for the formation constant of the ML complex by potentiometry. Polarography, on the other hand, worked very well when the total metal ion concentration was about 3×10^{-5} M and for ligand-to-metal ratios up to 1000. Under such conditions precipitation does not take place.

At all temperatures studied, the Pb-en-OH system behaved as a fully labile system. In Fig. 5, the shift in peak potential as a function of pH is presented for the sample studied at 5°C, and results recorded at this temperature are used to illustrate the way results obtained at all temperatures studied were interpreted.

More than 50 polarograms were recorded on one sample solution adjusted upward to the pH values indicated in Fig. 5. An increase in pH results in an increase in the free ligand concentration, owing to partial deprotonation of the ligand, and in a change in the solution composition, with formation of new species. From the shift in peak potential vs pH, an

electrochemical reaction is proposed that involves a species (a complex of a metal) believed to be present in the solution in a particular pH region. In Fig. 5, solid vertical lines separate pH regions where various metal ion-containing complexes are believed to predominate (one complex for each region). For each region the electrochemical process proposed also involves a predominant form of the ligand, obtained from consideration of the protonation constants in Table 1. The polarographic peak starts to shift above a pH value of about 6.8, and the slope reaches a constant value of about 27 mV per pH unit between pH 7.1 and 7.5. In this pH region the predominant form of the ligand is H_2L^{2+} . At 5°C, the term RT/nF is equal to about 55.16 mV, and since the number of electrons involved in the reduction of the Pb^{II} species at the mercury drop is two, the slope should be about 27.6 mV per pH unit per proton involved in the reaction at this temperature. It follows that a single proton is involved in the electrochemical process and the complex formed in this pH region is assigned as $Pb(HL)^{3+}$:



If the ML complex were to be formed in this pH region, then two protons would have to be involved in the electrochemical process and the slope observed should be close to 55 mV per pH unit, which is not the case.

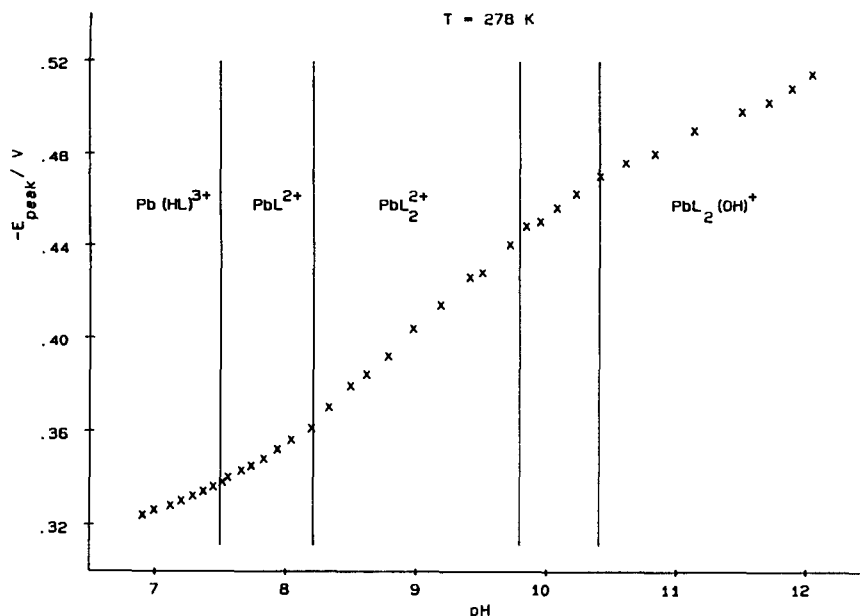
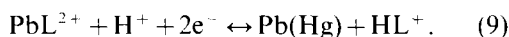


Fig. 5. Shift in differential pulse peak potential of lead complexes as a function of pH at 5 C. All polarograms were recorded on one solution sample, containing initially 2.49×10^{-5} M Pb^{2+} and 2.49×10^{-2} M en, adjusted to a particular pH to give data points indicated by \times . Solid vertical lines indicate boundaries between pH regions where an indicated complex is the predominant species.

In the pH range between 7.5 and 8.3, the slope in peak potential is constant and equal to about 32 mV per pH unit. At the same time, HL^+ becomes the major form of the ligand, with a still significant concentration of H_2L^{2+} . The value of the slope once again suggests an electrochemical process involving one proton, which means that in this pH region M(HL) is no longer the predominant species, since it would produce no change in peak potential with pH. The major species present here is assigned as the PbL^{2+} complex, which is involved in the reaction

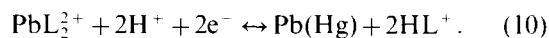


In support of the proposed ML complex, a Lingane approach can be used. The slope of the plot of ΔE_{peak} vs $\log[\text{L}]$ in this pH region should exhibit a constant value of about 27 mV per $\log[\text{L}]$ unit, which would indicate the formation of a metal complex involving one molecule of the ligand only.

This plot is shown on the left-hand portion of Fig. 6 and the slope observed is very close to the expected value of 27 mV per $\log[\text{L}]$. A slightly higher value than expected, i.e. 32 mV instead of 27.6 mV per pH unit (see Fig. 5, PbL^{2+} region) can be explained if it is noted that in this pH region the species H_2L^{2+} is also present in the solution and whereas reaction (9) is the major one, two protons can also be involved in this process to form H_2L^{2+} .

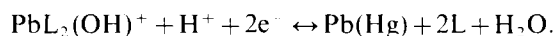
Between the pH values of 8.4 and 9.8, the slope of the peak potential vs pH plot in Fig. 5 has a

value of about 55 mV per pH unit and ΔE_{peak} vs $\log[\text{L}]$ has a constant value of about 55 mV per $\log[\text{L}]$ unit (see the right-hand portion of Fig. 6). This clearly indicates [see eq. (2)] that a PbL_2^{2+} complex is the major species present in the solution, and in this pH range the proposed electrochemical reaction is



Since the ligand is in the HL^+ form, two protons are required in the reaction above; this is in perfect agreement with the observed slope of 55 mV per pH unit.

At pH values of around 10, the shift in the peak potential with pH gradually decreases. This arises because the ligand is present in two forms, HL and L, with the concentration of L increasing when the pH value is increased. Above a pH value of about 10.4, the slope is established at a constant value of about 27 mV per pH unit. This can be explained by the formation of the $\text{ML}_2(\text{OH})^+$ complex. Its reduction at the mercury electrode requires a single proton when the ligand is present mainly in a fully deprotonated form, according to the reaction



To calculate formation constants for complexes of the form ML_b , a "standard" Lingane equation was used, the parameter b in eq. (2) being set equal to zero. For an M(HL) complex, the parameter b is

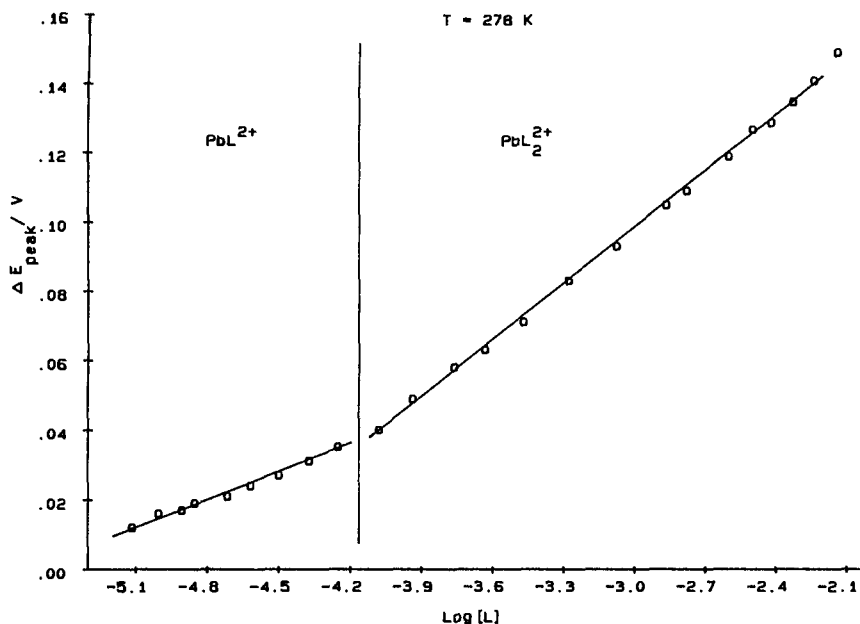


Fig. 6. Shift in differential pulse peak potential of Pb en^{2+} and Pb(en)_2^{2+} as a function of free ligand concentration in the pH range 7.5–9.8. Data points, indicated by \circ , are from the experiment illustrated in Fig. 5.

set equal to 1 and $\log[\text{OH}]$ is replaced by $\log[\text{H}]$ in eq. (2), and for $\text{ML}_f(\text{OH})_b$ complexes the equation was used as written. Polarographic results obtained at 25 and 50°C were interpreted in the same way. In Table 2 values of formation constants calculated in this work and elsewhere are presented.

It is interesting to note that the formation of species and their distribution as a function of pH varies with temperature (see Figs 7 and 8). Lead forms an $\text{M}(\text{HL})$ complex with the bidentate ligand en at 5°C. Previous studies, as well as our work, do not indicate the existence of this complex at 25°C and higher temperatures. The formation of singly coordinated lead complexes of the type $\text{Pb}^{2+}\text{-L-H}^+$ with a bidentate ligand might be surprising, but the indications are that lead does not gain much in stability from the chelate effect. It has, for example, been reported³⁰ that lead forms a $\text{Pb}(\text{H}_2\text{L})^{2+}$ complex with the ligand iminodiacetate, another example, presumably, of a singly coordinated lead complex involving a polydentate ligand. It is evident that at 5°C (the lowest temperature studied) the ML_2 complex is the predominant species and the $\text{ML}_2(\text{OH})_2$ complex is not formed at all up to a pH value of 13. With increase in temperature, an increase in the concentrations of the ML and $\text{ML}_2(\text{OH})_2$ complexes is observed. The ML complex is the main species at 50°C and intermediate pH values. At higher pH values, however, the $\text{ML}_2(\text{OH})_2$ complex is the predominant species and

not the ML_2 complex, which becomes almost a minor species.

The modified Lingane equation, when used to calculate a formation constant for a particular complex, yields a very constant value for that formation constant when calculations are done within the pH region where that complex is the predominant species. Although other species are present at the same time and their concentrations vary for each datum point, this seems to have a negligible effect on the calculated values of formation constants for the major species present in the solution. The above observation indicates that when one deals with a very labile system on the polarographic time scale, such as the Pb–en system, the reaction occurring at the mercury electrode surface involves mainly the major species. The moment the equilibrium at the electrode surface is disturbed by the electrochemical process, the other species react quickly to maintain equilibrium concentrations in the vicinity of the electrode. Electron transfer must be a slower process than chemical reaction or interconversion of labile complexes and if, for example, reduction of the ML complex requires slightly less energy than reduction of ML_2 , then the moment ML, the major species, is reduced the ML_2 complex dissociates to re-form ML complex rather than undergoing a reduction process itself. The same consideration applies to the protonation/deprotonation process of a ligand. The pH dependence of the elec-

Table 2. Formation constants for Pb^{II} complexes with en and hydroxide determined at an ionic strength of 0.1 M

Ligand	Equilibrium	Log β	Ref.
OH ⁻ at 5°C at 50°C	H ⁺ + OH ⁻ ⇌ H ₂ O	13.78	4
	H ⁺ + OH ⁻ ⇌ H ₂ O	14.48 ^a	this work
	H ⁺ + OH ⁻ ⇌ H ₂ O	13.02 ^a	this work
	Pb ²⁺ + OH ⁻ ⇌ Pb(OH) ⁺	6.0 ^b	4
	Pb ²⁺ + OH ⁻ ⇌ Pb(OH) ⁺	6.11 ^a	this work
	Pb ²⁺ + 2OH ⁻ ⇌ Pb(OH) ₂	10.3 ^b	4
	Pb ²⁺ + 2OH ⁻ ⇌ Pb(OH) ₂	10.46 ^a	this work
	Pb ²⁺ + 3OH ⁻ ⇌ Pb(OH) ₃ ⁻	13.3 ^b	4
en at 5°C	Pb ²⁺ + 3OH ⁻ ⇌ Pb(OH) ₃ ⁻	13.46 ^a	this work
	Pb ²⁺ + L + H ⁺ ⇌ Pb(HL) ³⁺	12.97(03)	this work
	Pb ²⁺ + L ⇌ PbL ²⁺	5.62(03)	this work
	Pb ²⁺ + 2L ⇌ PbL ₂ ²⁺	9.70(03)	this work
en at 25°C	Pb ²⁺ + 2L + OH ⁻ ⇌ PbL ₂ (OH) ⁺	13.45(1)	this work
	Pb ²⁺ + L ⇌ PbL ²⁺	5.05(03)	this work
	Pb ²⁺ + L ⇌ PbL ²⁺	5.04	4
	Pb ²⁺ + 2L ⇌ PbL ₂ ²⁺	8.67(03)	this work
en at 50°C	Pb ²⁺ + 2L + OH ⁻ ⇌ PbL ₂ (OH) ⁺	12.6(1)	this work
	Pb ²⁺ + 2L + 2OH ⁻ ⇌ PbL ₂ (OH) ₂	15.29(05)	this work
	Pb ²⁺ + L ⇌ PbL ²⁺	4.43(03)	this work
	Pb ²⁺ + 2L ⇌ PbL ₂ ²⁺	7.37(03)	this work
	Pb ²⁺ + 2L + OH ⁻ ⇌ PbL ₂ (OH) ⁺	11.75(05)	this work
	Pb ²⁺ + 2L + 2OH ⁻ ⇌ PbL ₂ (OH) ₂	14.8(1)	this work

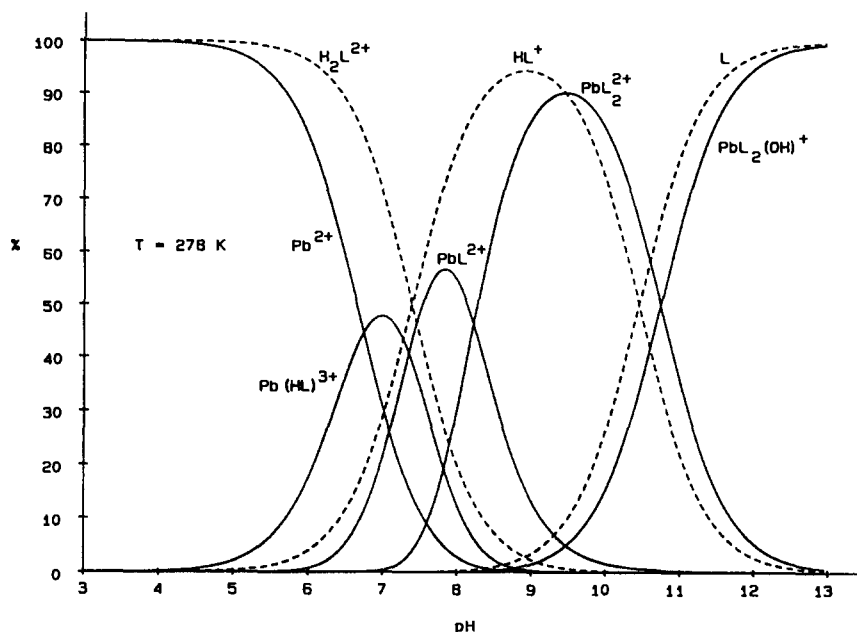
^aEstimated for an ionic strength of 0.1 M.^bIonic strength 0.3 M.

Fig. 7. The species distribution as a function of pH calculated for the Pb-en system at 5°C in the presence of 0.1 M sodium nitrate. $M_T = 1.9 \times 10^{-5}$ M; $L_T = 1.9 \times 10^{-2}$ M (—) fractions of the total lead concentration M_T ; (---) fractions of the total ligand concentration L_T in solution. The protonation constant of the ligand and formation constants for lead complexes with the ligand have been established in this work and are presented in Table 2.

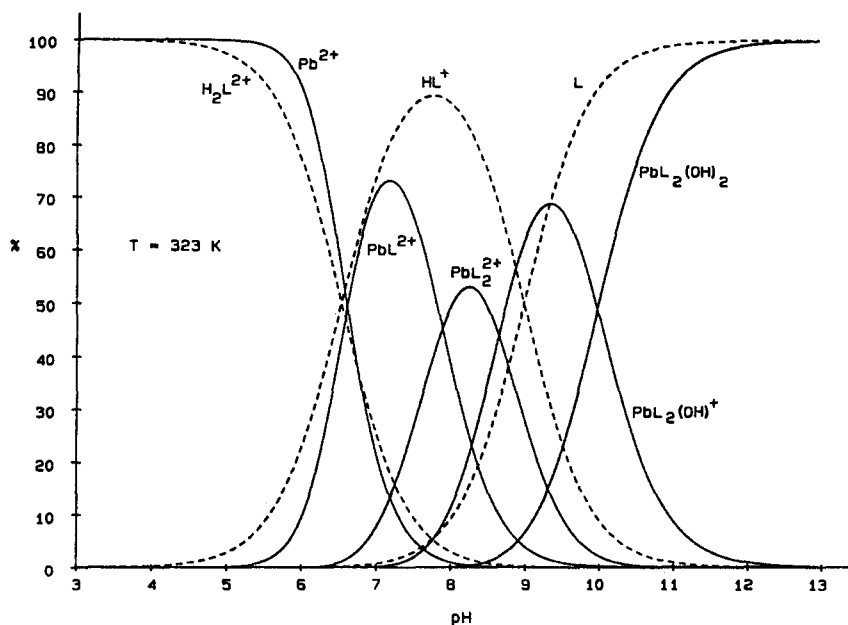


Fig. 8. The species distribution as a function of pH calculated for the Pb-en system at 50°C. Other details as for Fig. 7.

trochemical process is related to the predominant form of the ligand and not to other forms of the ligand present in the solution at the time.

This study also confirms that for labile complexes involving a protonatable ligand it is important to work with an excess total ligand, and not free ligand, concentration. The observed shift in peak potential for ML and ML_2 complexes as a function of $\log[L]$, here and for other systems,¹⁵⁻¹⁷ takes place in pH regions where the concentration of free ligand is far less than that of metal ion. Again, rapid dissociation of the excess protonated ligand is responsible for a constancy of free ligand concentration. As a result, the observed slope of ΔE_{peak} as a function of $\log[L]$ obeys the Lingane equation.

Calorimetric studies

Calorimetric titrations were carried out as outlined above (see Experimental). The calorimetric data were corrected for non-chemical heat effects such as heat exchange with the surroundings, heat of stirring, heat of dilution etc., essentially in the manner described by Eatough *et al.*³¹ Heat effects due to metal ion hydrolysis occurring to a small extent in the reaction vessel were corrected for, and the enthalpy changes for the metal-ligand complex formation reactions were calculated by use of the LETAGROP KALLE program.³² In these calculations the formation constants for complexes formed by Cd^{II} and Pb^{II} and the ligand THPED given in Table 1 were used to calculate con-

centrations of complex species formed at each datum point. The results obtained for ΔH° for the formation of the ML complexes are given in Table 3.

The calorimetric measurements were carried out under concentration conditions that were, of necessity, rather different from those prevailing in the potentiometric studies, with the result from too little $M(HL)$ and $ML(OH)$ were formed in the reaction vessel to allow reliable values of ΔH° for these species to be obtained.

Enthalpy changes for complex formation of Pb^{II} with en

From the values of formation constants determined by DPP at different temperatures for the Pb^{II} -en system (see Table 2), cumulative enthalpy changes for formation of the complexes PbL^{2+} , PbL_2^{2+} , $PbL_2(OH)^+$ and $PbL_2(OH)_2$ were deter-

Table 3. Enthalpy changes for complex formation of the metal ions Cd^{II} and Pb^{II} with the ligand $L = THPED$, determined at 25°C and ionic strength of 0.5 M

Metal ion	Reaction	ΔH° (kJ mol ⁻¹)
Cd^{2+}	$Cd^{2+} + L = CdL^{2+}$	-48 ± 2
Pb^{2+}	$Pb^{2+} + L = PbL^{2+}$	-48 ± 2

Table 4. ΔH° values for the complexes of Pb^{II} with en obtained by temperature dependence of formation constants determined by DPP at 5, 25 and 50°C

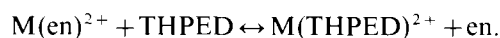
Reaction	ΔH° (kJ mol ⁻¹)
$\text{Pb}^{2+} + \text{L} = \text{PbL}^{2+}$	-44.7
$\text{Pb}^{2+} + 2\text{L} = \text{PbL}_2^{2+}$	-90.6
$\text{Pb}^{2+} + 2\text{L} + \text{OH}^- = \text{PbL}_2(\text{OH})^+$	-65.7
$\text{Pb}^{2+} + 2\text{L} + 2\text{OH}^- = \text{PbL}_2(\text{OH})_2$	-39.1 ^a

^aCalculated from two formation constants determined at 25 and 50°C.

mined from plots of $\log K$ vs $1/T$. Values obtained are given in Table 4.

CONCLUSIONS

The effect of addition of four 2-hydroxypropyl groups to en on the thermodynamics of complex formation can be discussed by reference to the ligand displacement reaction



Values of ΔG° , ΔH° and ΔS° for the above reaction are given in Table 5. It is evident that, in terms of the change in Gibbs function, addition of four 2-hydroxypropyl groups to en leads to a more stable complex for both Cd^{II} and Pb^{II} . The Pb^{II} complex is stabilized a little less than the Cd^{II} complex, which is perhaps a little surprising, since the ionic radius of the Pb^{2+} ion is a little larger than for Cd^{2+} ($r_{\text{Cd}^{2+}} = 0.95 \text{ \AA}$, $r_{\text{Pb}^{2+}} = 1.19 \text{ \AA}$, assuming a coordination number of six in both cases).³³ Even more surprising are the values of ΔH° for the ligand displacement reaction. It is seen that from an energetic standpoint, Pb^{II} has little to gain from addition of the 2-hydroxypropyl groups. Contrary to our

expectations, much of the extra stability of the THPED complex of Pb^{II} compared with the en complex is derived from the entropy contribution.

This apparent anomaly may relate to the extreme variability in coordination number for Pb^{II} complexes, which ranges³⁴ from four to ten in different complexes. It has been found³⁵ that Pb^{II} complexes with ligands of low denticity, such as $\text{R}-\text{N}(\text{CH}_2\text{CH}\cdot\text{CH}_3\text{OH})_2$, show an unusual tolerance towards bulky R groups not apparent for complexes of these ligands with any other metal ion. However, for Pb^{II} complexes with ligands of higher denticity, this tolerance disappears. One explanation may be that water molecules of hydration on Pb^{II} complexes are readily moved aside by bulky ligands. Another related explanation may be that with ligands $\text{R}-\text{N}(\text{CH}_2\text{CH}\cdot\text{CH}_3\text{OH})_2$ of low denticity, Pb^{II} has a stereochemically active lone pair and a lower coordination number (i.e. fewer coordinated water molecules), leading to tolerance of bulky alkyl groups. With ligands of higher denticity, the coordination number is larger (more coordinated water molecules) and the resulting steric crowding leads to greater sensitivity to bulky alkyl groups.

One would suggest here that the low enthalpy of complex formation of Pb^{II} with THPED relative to the en complex, leading to a value of ΔH° for the ligand displacement reaction that is more positive than expected by comparison with Cd^{II} , reflects different coordination numbers in the complexes $\text{Pb}(\text{en})^{2+}$ and $\text{Pb}(\text{THPED})^{2+}$. The only known complexes of Pb^{II} with an en coordinated to the Pb^{II} are seven-coordinate, which is a relatively low coordination number for a metal ion of the size of Pb^{II} . What is needed to resolve the question of the coordination numbers of the Pb^{II} complexes of en and THPED would be crystal structures of suitable complexes of Pb^{II} with both of these ligands.

Table 5. Values of ΔG° , ΔH° and ΔS° for ligand displacement reactions $\text{M}(\text{en})^{2+} + \text{THPED} \leftrightarrow \text{M}(\text{THPED})^{2+} + \text{en}$ ($\text{M} = \text{Cd}^{\text{II}}$ and Pb^{II}), obtained from appropriate combination of: (i) ΔG° values obtained from $\Delta G^\circ = -RT \ln \beta$ and formation constants from Tables 1 and 2; (ii) ΔH° values from Tables 3 and 4

Metal ion	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
Cd^{II}	-15.3	-22	-23
Pb^{II}	-13.8	-3	37

Values of ΔS° were calculated from $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$. A reported value of 5.4³³ was used for the formation constant for the $\text{Cd}(\text{en})^{2+}$ complex at 25°C and an ionic strength of 0.1 M, and a reported value of -25.9 kJ mol⁻¹³³ for ΔH° for the $\text{Cd}(\text{en})^{2+}$ complex at 25°C at an ionic strength of zero.

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