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# THERMOMETRIC STUDY OF METAL–NITROGENATED-LIGAND COMPLEXES. I. ETHYLENEDIAMINE COMPLEXES WITH Ag(I), Cu(II), Zn(II), Ni(II), Mn(II), Cd(II) AND Co(II)

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## ABSTRACT

The thermometric behaviour of a number of ethylenediamine complexes was studied from both analytical and physicochemical points of view.

Titration errors, calculated from different equivalent points, demonstrate the possible suitability of ethylenediamine as a titrant for Ag(I), Cu(II), Zn(II), Ni(II), Mn(II), Cd(II) and Co(II).

Overall complexation enthalpies were calculated and refined with the program MINITERM. The thermodynamic parameters $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ of several complexes are reported.

## INTRODUCTION

The great complexing capacity of the amine group is widely known and often selected as a starting point for studies of complexation [1].

Although potentiometric [2], spectrophotometric [3] and even conventional (batch) calorimetric studies [4] have been frequently used in the research of metal–nitrogenated-ligand complexes, thermometric titrations have seldom been applied to obtain thermodynamic values.

The latter technique has several advantages over other conventional calorimetric methods [5]: (1) it can be easily used for analytical purposes, taking advantage of the different slope changes of the enthalpograms caused by the successive complex formation; (2) valuable information about stoichiometries can be obtained by using very simple and cheap experimental techniques; (3) a great number of experimental points for enthalpy

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calculations can be obtained within a few minutes, contrasting with the long, time-consuming experiments involved in batch calorimetry; and (4) in some cases this technique allows simultaneous determination of all the main thermodynamic parameters, i.e. $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ (enthropic titrations) [6].

Thermometry is especially useful when uncoloured or insoluble complexes are formed. Such difficulties cannot be overcome by other classical techniques (i.e. potentiometry or spectrophotometry) [7].

In this first paper pyridine complexes were selected as a model system for complex formation with nitrogenated ligands, along with ethylenediamine, of interest owing to both its good complexing characteristics and high degree of solubility in water.

## EXPERIMENTAL

### *Apparatus*

An automatic thermometric system (described elsewhere [8]) was used. This system consisted of a Crison automatic burette connected to a portable IBM PC computer via a RS232C interface, an adiabatic cell, and a 100 KΩ thermistor connected to a Wheatstone bridge. The voltage output of this bridge was amplified (×10) and then measured by a digital potentiometer, which acted as an A/D converter and was connected via a RS232C interface to the computer. The computer controlled the overall system and stored the data [9].

### *Software*

A special program, VALTER*, was developed for data acquisition, representation and computing. This program, described elsewhere [8], stores and controls the experimental conditions (such as the volume of titrant to be added, addition speed, base-line stability, etc.), performs the titration tasks, acquires the data (which are then stored in an appropriate file), draws the titration curves and fits and extrapolates the linear intervals in order to identify the equivalent points.

To calculate the overall complexation enthalpies, the overall and point-by-point heat capacity methods [9] were used. The equation described later was applied for this purpose.

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* VALTER can be requested from SCIWARE, Department of Chemistry, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain.

TABLE 1

Reagents used

Pyridine (Probus) 1.233 M

Ethylenediamine (Probus) 1.0184 M; the reagent was previously titrated with $HClO_4$ in a non-aqueous medium

$AgNO_3$ 0.0510 N, stock solution

$CuSO_4$ 0.0527 M, titrated iodometrically

$Ni(NO_3)_2 \cdot 6H_2O$ 0.0527 M, Zn(II) 0.0791 M, $CdSO_4$ 0.0561 M, $Co(NO_3)_2 \cdot 6H_2O$ 0.0483 M and $MnSO_4$ 0.0486 M; all these solutions were standardized with EDTA

$NH_4Cl$–$NH_3$ buffer

Data files obtained with VALTER were appropriately modified for the MINITERM program [10], which allowed the refinement of the complex thermodynamic parameters (log $\beta$ and $\Delta H^0$).

### *Reagents*

Details of the reagents used in the present study are given in Table 1.

### *Procedure*

All titrations with ethylenediamine were carried out by placing the metallic ion in an appropriate (buffered or unbuffered) medium in the thermometric cell. The reagent was added when the sample mixture had reached thermal equilibrium, which was defined in the input experimental data conditions as the maximum base-line slope value allowed (0.001 °C $min^{-1}$).

Once the thermal stability criterion had been accomplished, the process of data acquisition was begun by first saving 10 consecutive points of the base line that fitted a straight line with a minimum correlation coefficient ($r \geqslant 0.999$) and then adding the titrant at a constant rate. As a great number of experimental post-equivalent point data were required for linear extrapolations and the MINITERM program [10], an excess of titrant was added in all cases.

## RESULTS

### *Standard model behaviour*

We chose the silver–pyridine complex reactions as a model system in order to check both the experimental and computing methods.

The same model has been frequently chosen for these purposes by other researchers [11] for a number of reasons:

(1) The equilibrium constants are expected to be independent of the ionic strength;

(2) side reactions may be omitted;

(3) the chemical system presents some degree of complexity;

(4) there are appropriate reference thermodynamic values in the literature which were calculated using very different techniques (solubility measurements [12], potentiometry [13–14], calorimetry [15–16], thermometry [17], etc.).

From the equilibria expressions and the matter and heat balances, eqns. (1)–(5) were deduced

$$\frac{c\,\Delta T(V_0+V_i)\left(1+\beta_1[\mathrm{Py}]_i+\beta_2[\mathrm{Py}]_i^2\right)}{V_0^2[\mathrm{Ag}^+]_0[\mathrm{Py}]_i\beta_1}=\Delta H_1+\frac{\beta_2}{\beta_1}[\mathrm{Py}]_i\,\Delta H_{\mathrm{T}} \qquad (1)$$

where $\beta_1$ and $\beta_2$ are the equilibrium constants of the complexes, $V_0$ is the initial volume of $\mathrm{Ag}^+$ in the cell, $V_i$ is the added volume of titrant (pyridine), $[\mathrm{Ag}]_0$ is the initial silver concentration, and $[\mathrm{Py}]_i$ is the free pyridine concentration at the $i$th point of the titration curve.

The $[\mathrm{Py}]_i$ values needed were calculated by means of the Newton–Raphson method applied to

$$\begin{aligned}&\beta_2(V_0+V_i)[\mathrm{Py}]_i^3-(\beta_2[\mathrm{Py}]_0V_i-\beta_1V_0-\beta_1V_i-2\beta_2[\mathrm{Ag}]_0V_0)[\mathrm{Py}]_i^2\\&\quad-([\mathrm{Py}]_0V_i\beta_1-\beta_1[\mathrm{Ag}]_0V_0-V_0-V_i)[\mathrm{Py}]_i-[\mathrm{Py}]_0V_i=0\end{aligned} \qquad (2)$$

The desired $\Delta H_1$ and $\Delta H_2$ values can be deduced from the intercept and slope of the linear representation of

$$Y=\Delta H_1+\Delta H_{\mathrm{T}}X \qquad (3)$$

obtained from eqn. (1) by substituting

$$Y=\frac{c\,\Delta T(V_0+V_i)\left(1+\beta_1[\mathrm{Py}]_i+\beta_2[\mathrm{Py}]_i^2\right)}{V_0^2[\mathrm{Ag}^+]_0[\mathrm{Py}]_i\beta_1} \qquad (4)$$

and

$$X=\frac{\beta_2}{\beta_1}[\mathrm{Py}]_i \qquad (5)$$

Results obtained when 80 ml of $6.394\times10^{-3}$ M $\mathrm{AgNO_3}$ were titrated with 1.233 M pyridine are shown in Table 2. Values of $\Delta T$ resulted from the difference between the experimental curves of the silver complexes and the blank (Fig. 1) corresponding to the pyridine heat of dilution.

Table 3 shows the averaged values found in different experiments.

A similar study was carried out with Cu(II) and pyridine with negative results caused by the badly shaped titration curves (Fig. 2). This difference with respect to the silver behaviour may be explained considering the acid

TABLE 2

Ag(I)–pyridine titration curve values

| $V_i$ (ml) | $\Delta T$(°C) | [pyr] | $X$ | $Y$ |
|---|---|---|---|---|
| 0.2142 | 0.0075 | 0.001747 | 0.28596 | 8.51778 |
| 0.2856 | 0.0102 | 0.002295 | 0.37596 | 9.58289 |
| 0.3570 | 0.0131 | 0.002812 | 0.46517 | 10.71202 |
| 0.4284 | 0.0155 | 0.003395 | 0.55562 | 11.51561 |
| 0.4998 | 0.0179 | 0.003957 | 0.64765 | 12.40358 |
| 0.5712 | 0.0205 | 0.004533 | 0.74181 | 13.50629 |
| 0.6426 | 0.0227 | 0.005124 | 0.83856 | 14.46302 |
| 0.7140 | 0.0250 | 0.005733 | 0.93826 | 15.51648 |
| 0.7854 | 0.0274 | 0.006362 | 1.04117 | 16.76121 |
| 0.8568 | 0.0296 | 0.007012 | 1.14752 | 18.01725 |
| 0.9282 | 0.0315 | 0.007684 | 1.25745 | 19.13941 |
| 0.9998 | 0.0332 | 0.008380 | 1.37135 | 20.31251 |
| 1.0710 | 0.0357 | 0.009095 | 1.48823 | 22.05947 |
| 1.1424 | 0.0375 | 0.009834 | 1.60917 | 23.46380 |
| 1.2138 | 0.0389 | 0.010594 | 1.73362 | 24.76164 |
| 1.2852 | 0.0407 | 0.011375 | 1.86149 | 26.46030 |
| 1.3566 | 0.0422 | 0.012177 | 1.99264 | 28.04763 |
| 1.4280 | 0.0436 | 0.012997 | 2.12689 | 29.64422 |
| 1.4994 | 0.0451 | 0.013836 | 2.26403 | 31.45116 |
| 1.5708 | 0.0461 | 0.014690 | 2.40386 | 33.01049 |
| 1.6422 | 0.0472 | 0.015560 | 2.54616 | 34.77038 |
| 1.7136 | 0.0482 | 0.016443 | 2.69071 | 36.51111 |
| 1.7850 | 0.0491 | 0.017339 | 2.83737 | 38.22139 |
| 1.8564 | 0.0501 | 0.018247 | 2.98588 | 40.16961 |
| 1.9278 | 0.0507 | 0.019165 | 3.13608 | 41.83194 |
| 1.9992 | 0.0517 | 0.020092 | 3.28779 | 43.83194 |
| 2.0706 | 0.0522 | 0.021027 | 3.44085 | 45.60226 |

Calorific capacity = 0.0893; pyridine concentration = 1.233 M; silver concentration = $6.394 \times 10^{-3}$ M.

Number of points, 27; slope $M = 11.8129 \pm 0.1202$; intercept $B = 4.6709 \pm 0.2349$; $R = 0.9997$; $E = 0.2881$.

B1 = 110; B2 = 18000.

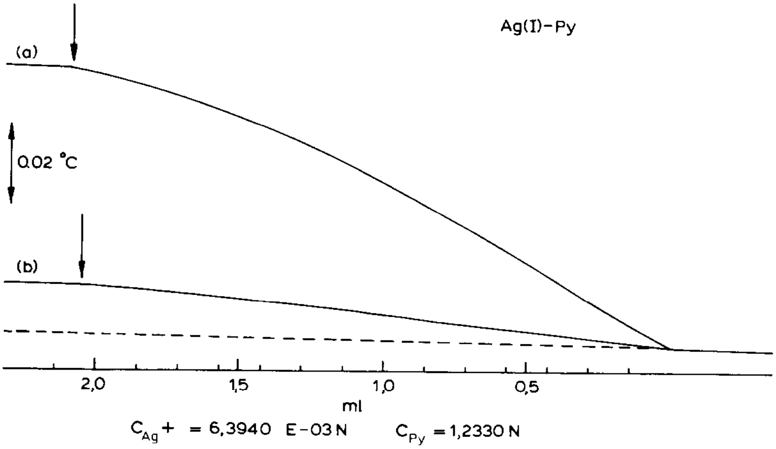

Fig. 1. (a) Enthalpogram of Ag(I)–pyridine complexes; (b) heat of dilution curve for pyridine.

TABLE 3

Thermodynamic parameters of Ag(I)–pyridine complexes

| Log $K_1$ | Log $K_2$ | $-\Delta G_1$ | $-\Delta G_2$ | $-\Delta H_1$ | $-\Delta H_2$ | $-\Delta S_1$ | $-\Delta S_2$ | References |
|---|---|---|---|---|---|---|---|---|
| 2.04 | 2.21 | 2.78 | 3.02 | 4.67 | 7.14 | 6.34 | 13.82 | This work |
| 2.00 | 2.11 | 2.73 | 2.89 | 4.83 ± 0.05 | 6.51 ± 0.06 | 7.0 ± 0.3 | 12.2 ± 0.5 | [15] |
| 2.04 | 2.08 | 2.78 | 2.83 | 4.6 ± 0.2 | 6.65 ± 0.09 | 6.2 ± 0.8 | 12.8 ± 0.8 | [17] |
| 2.06 | 2.12 | 2.81 | 2.89 | 4.73 ± 0.1 | 6.45 ± 0.01 | 6.4 ± 0.03 | 11.92 ± 0.03 | [18] |
|  |  |  |  | 4.6 ± 0.2 | 6.64 ± 0.12 | 6.0 ± 0.9 | 12.9 ± 0.4 | [17] |
| 1.93 | 2.29 | 2.63 | 3.12 | 4.6 | 6.6 | 6 | 13 | [19] |
| 2.24 | 1.95 | 3.06 | 2.66 | 4.77 | 6.76 | 5.7 | 13.8 | [16] |

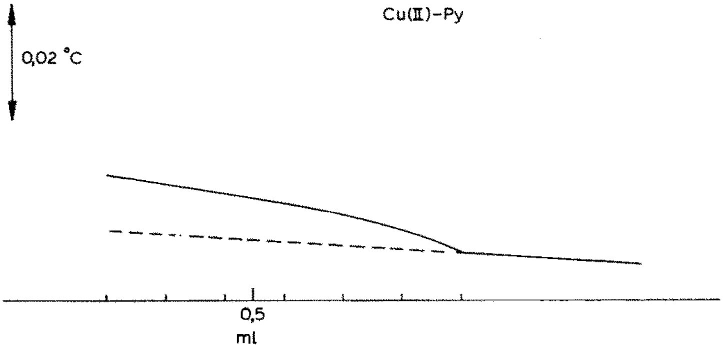

Fig. 2. Enthalpogram of Cu(II)–pyridine complexes. ($C_{Cu^{2+}} = 2.7410 \times 10^{-3}$ N; $C_{Py} = 1.2330$ N.)

character of the Cu(II) ions, whose hydrolysis introduces a side reaction of pyridine protonation, with consequent distortion of the enthalpogram.

## *Ethylenediamine complexes with metallic ions*

### *Stoichiometry and titration errors*

Enthalpograms show different shapes and stoichiometries, depending on the metallic ion considered. A number of the metallic ions studied gave

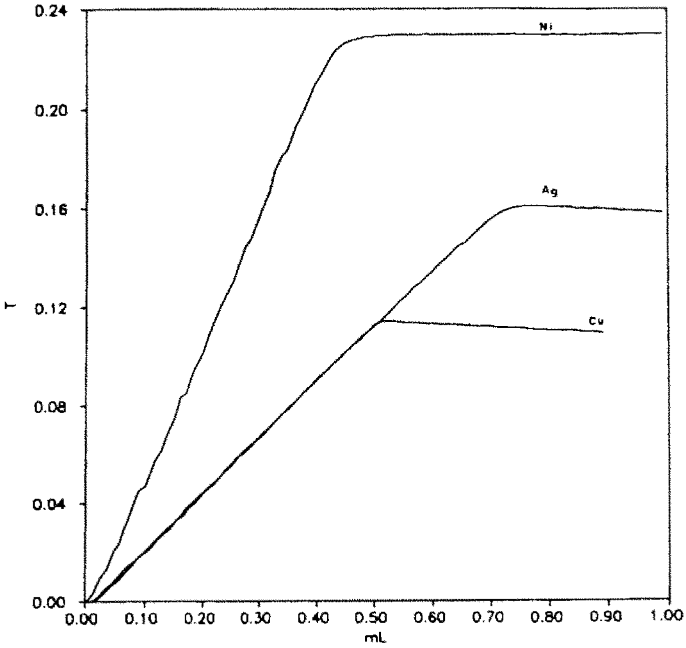

Fig. 3. Thermometric titration of Ag(I), Cu(II) and Ni(II) with ethylenediamine.

TABLE 4

Titration errors for the Ag(I), Cu(II) and Ni(II) complexes with ethylenediamine

| Actual quantity (mmol) | Quantity found automatically (mmol) | Error (%) | Quantity found manually (mmol) | Error (%) | Stoichiometry |
|---|---|---|---|---|---|
| Ag(I)–En | | | | | |
| 0.2550 | 0.2604 ± 0.004 | +2.12 | 0.2515 ± 0.007 | −1.40 | 1 : 1 |
| 0.3570 | 0.3503 ± 0.008 | −1.88 | 0.3460 ± 0.051 | −1.34 | 1 : 1 |
| 0.5100 | 0.5082 ± 0.006 | −0.35 | 0.5090 ± 0.004 | −0.20 | 1 : 1 |
| 0.6120 | 0.5954 ± 0.008 | −2.70 | 0.5885 ± 0.004 | −3.84 | 1 : 1 |
| 0.7650 | 0.7441 ± 0.008 | −2.73 | 0.7395 ± 0.004 | −3.33 | 1 : 1 |
| Cu(II)–En | | | | | |
| 0.2635 | 0.2556 ± 0.002 | −3.00 | 0.2595 ± 0.004 | −1.52 | 1 : 2 |
| 0.3689 | 0.3653 ± 0.001 | −0.98 | 0.3659 ± 0.003 | −0.81 | 1 : 2 |
| 0.5270 | 0.5248 ± 0.002 | −0.42 | 0.5213 ± 0.002 | −1.07 | 1 : 2 |
| 0.6324 | 0.6151 ± 0.004 | −2.73 | 0.6162 ± 0.003 | −2.56 | 1 : 2 |
| 0.7905 | 0.7784 ± 0.003 | −1.53 | 0.7721 ± 0.003 | −2.33 | 1 : 2 |
| Ni(II)–En | | | | | |
| 0.7275 | 0.7303 ± 0.002 | −0.40 | 0.7249 ± 0.010 | −0.35 | 1 : 3 |
| 1.0185 | 1.0429 ± 0.016 | +2.34 | 1.0174 ± 0.014 | −0.11 | 1 : 3 |
| 1.4550 | 1.4596 ± 0.026 | +0.30 | 1.4535 ± 0.013 | −0.16 | 1 : 3 |
| 1.7460 | 1.7366 ± 0.031 | −0.54 | 1.7286 ± 0.017 | −0.10 | 1 : 3 |
| 2.1825 | 2.1534 ± 0.030 | −0.13 | 2.1268 ± 0.006 | −0.99 | 1 : 3 |

well-defined titration curves, with only one sharp change in slope, thus allowing automatic end-point determination by means of the program VALTER, with similar errors to those obtained when this was done manually.

In Fig. 3 the thermometric titration curves for Ag(I), Cu(II) and Ni(II) with ethylenediamine are shown, where their sharp end points correspond, respectively, to 1 : 1, 1 : 2 and 1 : 3 stoichiometries. Both manual and automatic titration errors are given in Table 4.

For Co(II), Zn(II), Cd(II) and Mn(II), the enthalpograms not only present one sharp end point, but also a number of slight slope changes, which correspond to complexes with different stoichiometries. Therefore, automatic end-point determination could not be carried out.

Figure 4 shows the shapes of these curves and Table 5 presents the errors, calculated manually, for the different stoichiometries of each ion.

The unfavourable log $\beta_3$ values of the remaining cations lead to rounded titration curves, hindering linear extrapolation for end-point determination.

In all the cases, titration errors were found to be less when the slope change was sharper. Hence, the sharpest slope variation for Zn(II), corresponding to the 1 : 2 stoichiometry, gave the minimum titration error. The same behaviour was found for Cd(II), Co(II) and Mn(II).

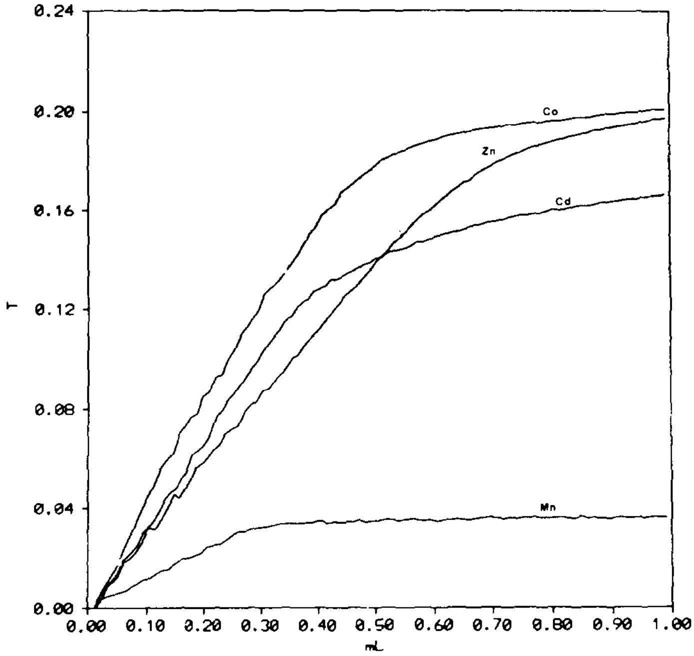

Fig. 4. Thermometric titration of Cd(II), Co(II), Mn(II) and Ni(II) with ethylenediamine in unbuffered medium.

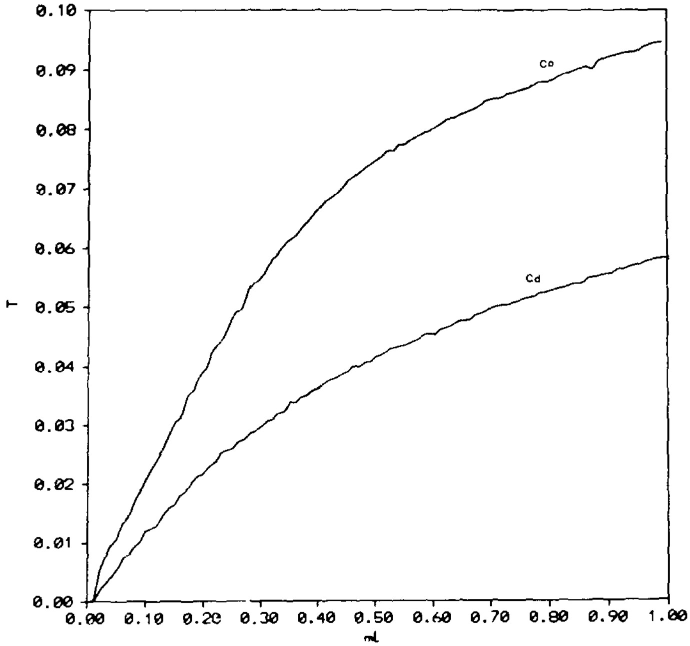

Fig. 5. Thermometric titration of Cd(II) and Co(II) with ethylenediamine in buffered medium ($NH_4Cl-NH_3$, pH = 10).

TABLE 5

Titration errors for the Zn(II), Cd(II), Co(II), and Mn(II) complexes with ethylenediamine in an unbuffered medium

| Metal | No. of expts. | Quantity of metal (mmol) | Quantity of en found (mmol) | Error (%) | Stoichiometry |
|---|---|---|---|---|---|
| Zn(II) | 4 | 0.7910 | 0.5734 ± 0.040 | −27.50 | 1:1 |
| | | | 1.6179 ± 0.179 | −2.27 | 1:2 |
| | | | 2.1867 ± 0.049 | −7.85 | 1:3 |
| Cd(II) | 3 | 0.5610 | 0.4745 ± 0.089 | −15.40 | 1:1 |
| | | | 1.1103 ± 0.046 | −1.04 | 1:2 |
| | | | 1.8292 ± 0.158 | +8.70 | 1:3 |
| Co(II) | 3 | 0.4830 | 0.3852 ± 0.046 | −20.25 | 1:1 |
| | | | 0.9196 ± 0.051 | −4.80 | 1:2 |
| | | | 1.4944 ± 0.013 | +3.13 | 1:3 |
| Mn(II) | 2 | 0.2430 | 0.2262 ± 0.045 | −6.90 | 1:1 |
| | | | 0.5475 ± 0.026 | +12.65 | 1:2 |
| | | | 0.7063 ± 0.008 | −3.11 | 1:3 |
| | 2 | 0.4860 | 0.3811 ± 0.092 | −21.60 | 1:1 |
| | | | 0.9396 ± 0.011 | −3.30 | 1:2 |
| | | | | | 1:3 |
| | 2 | 0.7290 | 0.4910 ± 0.044 | −3.26 | 1:1 |
| | | | 1.0702 ± 0.073 | −26.60 | 1:2 |

In order to avoid possible reagent protonation caused by the hydrolysis of metallic ions, thermometric titrations were repeated in buffered media. Thus, Zn(II), Cd(II), Co(II) and Mn(II) were titrated with ethylenediamine ($pK_1 = 7.31$, $pK_2 = 10.04$) in a buffered medium ($NH_4Cl$–$NH_3$, pH = 10).

Using this buffer, no titration curve for Zn(II) and Mn(II) was observed. Only a slight temperature increment took place which was due to the ethylenediamine heat of dilution. Enthalpograms of Cd(II) and Co(II) in a buffered medium are shown in Fig. 5.

For the buffered 1 : 3 ethylenediamine–Cd(II) complex the slope change was sharper than those in the unbuffered medium. As a result, titration

TABLE 6

Titration errors for Cd(II) and Co(II) complexes with ethylenediamine in a buffered medium ($NH_4Cl/NH_3$, pH = 10)

| Metal | No. of expts. | Quantity of metal (mmol) | Quantity of en found (mmol) | Error (%) | Stoichiometry |
|---|---|---|---|---|---|
| Cd(II) | 3 | 0.5610 | 0.4121 ± 0.158 | −26.43 | 1:1 |
| | | | 0.8730 ± 0.089 | −22.01 | 1:2 |
| | | | 1.6679 ± 0.038 | −1.25 | 1:3 |
| Co(II) | 3 | 0.4830 | 0.4926 ± 0.056 | +1.98 | 1:1 |
| | | | 0.9767 ± 0.079 | +1.11 | 1:2 |
| | | | 1.6404 ± 0.203 | +9.43 | 1:3 |

TABLE 7

Calculated and literature values of thermodynamic parameters for pyridine and ethylenediamine complexes

| Complex | Stoichiometry | Log $\beta_i$ (calc.) | $\Delta H_i$ (calc.) (Kcal mol$^{-1}$) | log $\beta_i$ (lit.) | $\Delta H_i$ (lit.) (Kcal mol$^{-1}$) |
|---|---|---|---|---|---|
| Ag–Py | 1:1 | 2.07 | −4.87 | 2.06 | −4.78 |
| | 1:2 | 4.17 | −12.36 | 4.18 | −11.26 |
| Ag–En | 1:1 | 4.68±0.01 | [a] | 4.70 | – |
| | 1:2 | 7.69±0.00 | −12.57±0.70 | 7.70 | – |
| | 2:2 | 13.19±0.00 | −27.07±0.28 | 13.23 | – |
| Cu–En | 1:1 | 10.56±0.03 | −13.04±0.75 | 10.54±0.1 | −13.1±0.2 |
| | 1:2 | 19.60±0.05 | −25.77±1.18 | 19.60±0.2 | −25.5±0.2 |
| Ni–En | 1:1 | 7.35±0.04 | −8.76±0.18 | 7.35±0.1 | −9.0±0.1 |
| | 1:2 | 13.54±0.03 | −18.86±0.47 | 13.54±0.1 | −18.3±0.1 |
| | 1:3 | 17.71±0.01 | −28.17±0.29 | 17.71±0.1 | −28.0±0.1 |
| Zn–En | 1:1 | 5.69±0.00 | −5.85±0.09 | 5.70±0.1 | −7.0 |
| | 1:2 | 10.62±0.00 | −11.00±0.23 | 10.62±0.02 | −11.9 |
| | 1:3 | 13.24±0.01 | −15.35±0.39 | 13.23 | −17.1 |
| Cd–En | 1:1 | 5.45±0.01 | −6.82±0.06 | 5.45±0.1 | −6[b] |
| | 1:2 | 9.98±0.00 | −15.81±0.43 | 9.98 | −13.3[b] |
| | 1:3 | 11.74±0.00 | −20.50±0.38 | 11.74 | −19.7[b] |
| Co–En | 1:1 | 5.63±0.02 | −9.51±0.18 | 5.6 ±0.3[b] | −6.9 |
| | 1:2 | 10.44±0.04 | −15.81±0.43 | 10.50±0.3 | −14.0 |
| | 1:3 | 13.81±0.01 | −23.33±0.13 | 13.78 | −22.2 |
| Mn–En | 1:1 | 2.76±0.02 | −3.46±0.76 | 2.77 | −2.8 |
| | 1:2 | 4.87±0.01 | −5.90±0.22 | 4.87 | −6.0 |
| | 1:3 | 5.76±0.04 | – | 5.81 | −11.1 |

[a] Unreproducible value.

[b] Approximate.

errors decreased for this complex. Conversely, in the cases of Cd(II) 1 : 1 and 1 : 2 not only did the results not improve, but the errors increased (Tables 5 and 6).

Titration errors for Co(II) in a buffered medium decreased for 1 : 1 and 1 : 2 complexes, whereas they increased for the 1 : 3 complex owing to enthalpogram rounding around the end-point interval.

### *Complexation enthalpies*

Data files acquired by the VALTER program were slightly modified with the WORDPERFECT editor for direct refinement of the thermodynamic parameters (log $\beta_i$, $\Delta H_i$) by the MINITERM program.

Results are summarized in Table 7. The formation enthalpy of the 1 : 3 ethylenediamine–Mn(II) complex could not be obtained owing to its low formation constant.

Irreproducible values resulted from studies of the enthalpy of the 1 : 1 ethylenediamine–Ag(I) complex. Residuals, however, dramatically decreased when a binuclear 2 : 2 complex was taken into account.

In the cases of the other cations considered in this work, the results obtained agreed with those of the literature.

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