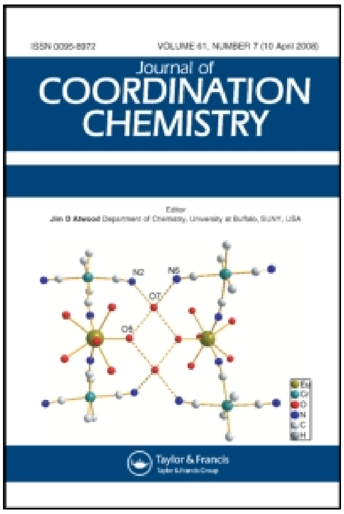

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A RE-INVESTIGATION OF THE THERMODYNAMICS OF FORMATION OF COMPLEXES OF NICKEL(II) WITH 2,2'-OXYBISETHANAMINE AND 2-(2-AMINOETHYL) AMINOETHANOL

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A RE-INVESTIGATION OF THE THERMODYNAMICS OF FORMATION OF COMPLEXES OF NICKEL(II) WITH 2,2'-OXYBISETHANAMINE AND 2-(2-AMINOETHYL) AMINOETHANOL

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The thermodynamics of complexation of the ligands 2,2'-oxybisethanamine (oden) and 2-(2-aminoethyl)aminoethanol (etolen) with the Ni^{2+} ion were re-investigated by glass electrode potentiometry and titration calorimetry at 25°C and in 0.5 mol dm^{-3} KNO_3. In the case of the ligand etolen the data were consistent with previously reported complexes, $Ni(etolen)^{2+}$ and $Ni(etolen)_2{}^{2+}$, and associated stability constants. However, the enthalpies of complexation obtained here differ from those previously reported. Reasons for these discrepancies are discussed. For the ligand oden the data could only be explained by the inclusion of the ternary species $Ni(oden)OH^+$ and $Ni(oden)_2OH^+$ in addition to the binary species $Ni(oden)^{2+}$ and $Ni(oden)_2{}^{2+}$. Thermodynamic parameters of complexation for these complexes are reported and compared with those of the etolen complexes.

KEYWORDS: nickel, polyamines, stability constants, thermochemical parameters

INTRODUCTION

Hancock, McDougall and Marsicano[1] asserted that, in the absence of ring strain effects, the formation of nickel-secondary nitrogen bonds is enthalpy-stabilized, compared with nickel-primary nitrogen bonds. The higher donor strength of nitrogens as one moves along the series zeroth (ammonia) < primary < secondary < tertiary has been used as an explanation for the high ligand field strength exhibited by some tetraazamacrocycle complexes.[2-3]

As the assertion of Hancock et al.[1] had been deduced from strain energy calculations performed on nickel polyamine complexes, it seemed pertinent to test it experimentally. An appropriate pair of ligands with which to carry out this aim was 2,2'-oxybisethanamine [oden $\equiv (H_2NCH_2CH_2)_2O$] and 2-(2-aminoethyl) aminoethanol [etolen $\equiv HO(CH_2)_2NH(CH_2)_2NH_2$].

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Values of ΔG°, ΔH° and ΔS° for the formation of complexes involving oden and etolen with Ni^{2+} have been reported[4,5] with a view to evaluating the coordinating properties of the oxygen atom. However, these values are in poor accord with previously reported values[6,7] for the same quantities and, in addition, the existence of only ML_n type complexes was considered. It therefore seemed important to re-determine the thermodynamic data relating to the complexation of Ni^{2+} with the ligands oden and etolen.

The stability constants (and hence ΔG°) of the reactions studied were determined by glass electrode potentiometry and the enthalpy changes by titration calorimetry. All measurements were made at an ionic strength of 0.5 mol dm^{-3} using KNO_3 as the background electrolyte, and at a temperature of 25°C.

EXPERIMENTAL

Materials

Only A-grade volumetric glassware and doubly deionized water were used in the preparation of solutions. Nitric acid (Merck p.a.) solutions were standardized by titration against freshly recrystallized borax.[8] Stock solutions of sodium hydroxide (*ca* 1 mol dm^{-3}) were prepared from Merck TITRISOL concentrated volumetric solutions and were made up to volume with water which had been twice deionized and freshly boiled to expel CO_2. When these ampoules were not available the stock solutions were prepared by dilution of a 50% NaOH solution, as described by Vogel.[9] In both cases, the solutions prepared from these stock solutions were standardized by potentiometric titration against a standard nitric acid solution, and application of the Gran method[10] of end-point detection. Stock solutions of the background electrolyte, potassium nitrate, were prepared by mass from BDH Analar reagent. These solutions were periodically standardized by passing aliquots through a cation exchange resin (BDH Amberlite IR-120 (H)) and titrating the resulting HNO_3 eluate against a freshly prepared and standardized NaOH solution with methyl orange as indicator. The concentration of KNO_3 obtained in this way differed from that calculated by mass by only 0.4%, which is not significant for a background electrolyte. Nickel nitrate (Merck p.a.) stock solutions were standardized by direct titration against a standard solution of ethylenediaminetetraacetic acid (Merck p.a.) with murexide as indicator.[11]

The 2-(2-aminoethyl)aminoethanol ligand (Riedel-de Haën, Prosynth grade) used was purified by fractional distillation under reduced pressure. The fraction used distilled over at 89°C, at 0.9 mmHg. Solutions of this amine were prepared by using freshly boiled, doubly deionized water, and standardized a day before use. The concentrations of the solutions were determined by potentiometric titration against a standard nitric acid solution. End-points were determined by using an 'extended' Gran plot method adapted for a weak diprotic base from the method devised by Ingman and Still.[12]

The ligand 2,2'-oxybisethanamine was purchased as the dihydrochloride from Aldrich, purified by recrystallization from hot aqueous ethanol and dried to constant mass. The melting point of the recrystallized material was found to be 226.0-226.5°C, which compared well with the published value of 226–227°C.[13] Solutions of oden.2HCl were prepared fresh as required, by using boiled, decarbonated, doubly deionized water. These were standardized by potentiometric titration against a standard sodium hydroxide solution using the Gran plot method of end-point detection for dibasic acids.[10b]

Potentiometric Apparatus

The potentiometric titrations were performed in a jacketed glass reaction vessel (Metrohm No. EA 876-50) thermostatted at 25.00±0.05°C by water circulating from a constant temperature bath. The emf of the cell was measured to ±0.1 mV with Radiometer PHM 64 and PHM 84 research pH meters equipped with Radiometer G202B (low sodium error) glass electrodes and Metrohm type EA-275 silver-silver chloride reference electrodes. The reference electrode and salt bridge was assembled by using two INGOLD liquid junction tubes, type 303/95/T/NS, which were modified so that the assembly could be thermostatted in the same way as the reaction vessel. Sodium hydroxide titrant was dispensed from a Mettler automatic burette where the reservoir had been modified to keep the solution under a constant atmosphere of nitrogen. A stream of high purity nitrogen, which had been freed from acid and alkaline impurities by passage through 10% NaOH and 10% H_2SO_4 solutions, respectively, and then presaturated with 0.5 mol dm^{-3} KNO_3, was bubbled through the test solution during the entire duration of the experiment. The solution in the cell was stirred magnetically at all times. Potentiometric titrations were performed in a room thermostatted at 25±1°C.

Calorimetric Apparatus

Enthalpy changes were measured by means of a precision titration calorimeter. The construction and testing of the calorimeter have been previously described.[14] The titration calorimeter consists essentially of the LKB 8721-2 titration calorimeter assembly with an electronic system designed and constructed by the Council for Mineral Technology. Since the report on the construction of the calorimeter was published, some changes have been made to the electronic assembly.[15] The calorimeter was housed in a room thermostatted at 25±1°C.

Potentiometric Procedure

The potentiometric cell used is as follows,

Ag|AgCl|salt bridge| test solution| glass electrode

in which the reference electrode solution was 0.01 mol dm^{-3} Cl^-, 0.49 mol dm^{-3} NO_3^- and 0.50 mol dm^{-3} K^+ and the salt bridge consisted of 0.50 mol dm^{-3} KNO_3. This cell was calibrated *in situ* in terms of hydrogen ion concentration at the start of each titration. In these calibrations the ionic product of water in the medium was assumed to be constant and either the glass electrode response was assumed to be Nernstian and only the standard cell emf, E°, was determined, or both the slope and E° for the electrode calibration line was determined.

Complexation equilibria were studied at several metal ion concentrations and several ligand-to-metal ion concentration ratios. The various experimental conditions are listed in Table 1.

Table 1 Experimental conditions used for the potentiometric titrations.

Titration number	[etolen]/ mmol dm^{-3}	[oden]/ mmol dm^{-3}	[Ni^{2+}]/ mmol dm^{-3}	Ligand-metal ratio	p[H^+] range
1	5.569		2.501	2.2	7.2-2.8
2(a)	11.19		2.501	4.5	7.2-3.3
2(b)	8.954		2.501	3.6	4.9-10.1
3(a)	5.569		0.5011	11.1	7.9-2.7
3(b)	4.243		0.5009	8.5	3.0-11.2
4	10.22		3.334	3.1	5.2-7.2
5	10.66		1.739	6.1	5.3-7.6
6	10.22		2.499	4.1	5.2-7.3
7	10.22		3.334	3.1	5.2-7.4
1(a)		2.175	0.9793	2.2	7.7-10.0
1(b)		1.667	0.9824	1.7	9.5-7.7
2		4.485	1.001	4.5	6.9-10.2
3		4.485	0.5007	9.0	7.6-10.4
4		10.00	5.000	2.0	6.9-8.9
5		10.00	1.667	6.0	7.1-9.3
6		6.668	1.667	4.0	7.1-9.3
7		10.09	5.042	2.0	7.1-8.7

For the nickel-etolen system, titrations 1–3 were performed by starting with the complex ion in solution and stripping the ligand off the metal ion with acid. In these titrations the potentiometric cell was calibrated with strong acid alone and only E° was determined. In titrations 2 and 3, the reversibility of the equilibria was tested by performing both forward (decreasing p[H^+]) and reverse (increasing p[H^+]) titrations (titrations were reversed by titrating the reaction mixture with a solution of NaOH). The total metal ion concentration was kept constant in titrations 1–3.

For the nickel-oden system titrations nos. 1–3 were carried out by adding a hydroxide-containing titrant solution to a titrate containing Ni^{2+} and oden.2HCl. In these titrations the potentiometric cell was calibrated with strong acid and strong base. The Gran plot method was used to determine the hydroxide concentration as well as the amount of carbonate impurity present. The speciation program HALTAFALL[16] was used to calculate the p[H^+] value at each titration point in the calibration and thence both E° and the slope were determined. In the first titration the total concentration of Ni^{2+} was kept constant. In addition, the reversibility of the reactions was tested by performing a reverse titration (decreasing p[H^+]) once the forward titration had been completed. This was achieved by adding a titrant solution containing hydrogen ion.

For both systems studied, in the remainder of the titrations (nos. 4-7) the cell was calibrated with strong acid and the ligand as a weak base. The p[H^+] at each titration point was calculated from the reagent concentrations and the protonation constants of the ligand with the aid of HALTAFALL. The resulting p[H^+] and emf data were then used to determine both the slope and E°. Here a titrant solution containing ligand was added to a reaction mixture containing Ni^{2+}, doubly protonated ligand and surplus acid. In this way protonated ligand was always present as part of the background electrolyte and so helped to lower the working p[H^+] and possibly to suppress hydrolysis of the metal-ligand complexes. One titration (no. 4) was carried out in duplicate in order to check the reproducibility of the results obtained. The repeat titration is no. 7 in both cases.

Calorimetric Procedure

The calorimetric titrations involving etolen and Ni^{2+} were designed so that a titrant solution containing ligand was added to a titrate solution containing metal ion, some doubly protonated ligand and some surplus acid. In this way approximately 30% of the background electrolyte was replaced by the nitrate salt of the doubly protonated ligand, which lowered the $p[H^+]$ and suppressed hydrolysis of the metal-ligand complexes. For this system all the calorimetric measurements were carried out in triplicate. This included the heat capacities of all the solutions, blank titrations to determine the heat of dilution of the titrant as it is added to the titrate, and the actual titrations involving the reactants.

The high cost of the ligand oden prevented the use of concentrated ligand solutions in the calorimetric titrations. These titrations were therefore performed by titrating a solution of the metal ion into a solution containing a mixture of ligand and protonated ligand. The heat capacities of the solutions and the heat of dilution were determined in triplicate. The heat of reaction titration was carried out in quadruplicate. Initial calorimetric experiments performed with oden involved the titration of the metal ion into a dilute solution of the deprotonated ligand. However, this gave rise to the formation of an undesirable precipitate in the reaction vessel and this line was not pursued.

Data Treatment

The formation of metal complexes from a metal ion M, a ligand L and a proton H, can be represented by the following equation. The associated cumulative stability constant is denoted β_{pqr}. In the analysis of the potentiometric data the protonation constants of the ligands and the stability constant for the hydrolysis of Ni^{2+} were regarded as known and kept constant. The values used are listed in Table 2. The data were processed with the ESTA set of programs.[21,22]

$$pH(aq) + qM(aq) + rL(aq) \rightleftharpoons H_pM_qL_r(aq)$$

Table 2 Constants used in the calculation of stability constants and enthalpy changes. All data are for 25°C and μ = 0.5 mol dm^{-3}, except where indicated.

Reaction	log β	$\Delta H°$/kJ mol^{-1}	Reference
$H_2 \rightleftharpoons H^+ + OH^-$	-13.74	56.69	17
H^+ + etolen $\rightleftharpoons$ Hetolen$^+$	9.74	-47.0	15
H^+ + Hetolen$^+$ $\rightleftharpoons$ H_2etolen^{2+}	6.85	-41.6	15
H^+ + oden $\rightleftharpoons$ Hoden$^+$	9.77	-50.2	15
H^+ + Hoden$^+$ $\rightleftharpoons$ H_2oden^{2+}	9.17	-53.4	15
$Ni^{2+} + H_2O \rightleftharpoons Ni(OH)^+ + H^+$	-10.15[a]	32.47[b]	18,19

[a] Corrected from μ = 0.1 mol dm^{-3} to μ = 0.5 mol dm^{-3} with the Davies equation [20]. [b] Value for μ = 1.0 mol dm^{-3}.

Results were displayed graphically by means of formation curves, $\overline{Z}_M(\log A)$, where the complex formation function $\overline{Z}_M$ is defined by the following two equations.

$$\overline{Z}_M = \frac{[L]_t - A\left(1 + \sum_{n=1}^{n} \beta_{no1}[H^+]^n\right)}{[M]_t}$$

$$A = \frac{[H^+]_t - [H^+] + [OH^-]}{\sum_{n=1}^{n} \beta_{no1}[H^+]^n}$$

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. Complex formation curves are useful for ascertaining the species that are likely to be formed in solution.

In this work the shapes of the formation curves were used to infer the nature of the major species formed in the systems studied. Various sets of minor species were then tested. These minor species were included in the initial model either singly, in pairs, or triply. The likely models were tested by making use of the BETA task in the ESTA program which allows the calculation of individual complex species. With the BETA task a number of these models can be tested simultaneously. From the output provided by BETA one can consider for inclusion in the model the minor species which best satisfy the following criteria[23] (i) the minor species should be present at a large number of titration points, (ii) the stability constant calculated for the minor species should not vary much, and (iii) the calculated concentration of the minor species should change appreciably from point to point, and its percentage formation should lie between 15% and 85%. Formation constants for the species present in the most likely models were then refined by using the OBJE optimization module of ESTA in which the objective function is defined in terms of the cell emf. The adequacy of each model tested was evaluated by consideration of the value of the objective function. That model which yields the lowest value of the objective function gives the best fit to the experimental data. Where several models had very similar values for the objective function the simplest model was chosen, in keeping with Occam's Razor. The adequacy of the models eventually selected to describe the solution equilibria was also assessed visually by comparing plots of $\overline{Z}_M$(obs) and $\overline{Z}_M$ (calc), the former calculated from experimentally determined values of $[H^+]$ and the latter from values of $[H^+]$ calculated on the basis of the model tested. If any serious discrepancies occurred, other models were tried.

The calorimetric data were corrected for non-chemical heat effects essentially in the manner described by Eatough *et al.*[24] The enthalpy changes were calculated from these 'corrected' heats by use of the LETAGROP KALLE program.[25] In the case of calorimetric experiments performed with etolen the data were corrected for the initial protonation of the ligand from the titrant by the surplus acid present in the titrate.

RESULTS AND DISCUSSION

The formation curves for the Ni-etolen system were, within estimated experimental error, superimposable for $\bar{Z}_M$ values between 0 and 2. Since the metal ion concentration was varied, and repeat and reverse titrations were performed, one can conclude that no polynuclear species are present, the results are reproducible, and the equilibria are reversible.

Because the highest reliable value of $\bar{Z}_M$ reached was approximately 2, and there was evidence of a plateau at this value, the highest major mononuclear complex formed was taken to be ML_2. Also, the formation curves are fairly symmetrical under rotation about the point with $\bar{Z}_M = 1$, which suggests that only two major species, *viz*, ML and ML_2, are present. Attempts were made to introduce various minor species into the model, but with no success.

During the calculation of the stability constants for this system, fixed values of the stability constants for the species H_2O, HL^+, H_2L^{2+} and Ni $(OH)^+$, as given in Table 2, were used. The results obtained, together with pertinent values reported in the literature, are shown in Table 3.

The $\bar{Z}_M$(calc) curve derived from these results agrees fairly well with the experimental formation curves. Hence it was concluded that the complexes Ni(etolen)$^{2+}$ and Ni(etolen)$_2^{2+}$ adequately account for the potentiometric observations. Stability constants obtained for this system agree well with those reported in references 26 and 27 and were obtained under similar experimental conditions. However, they do not agree well with those obtained by Hall *et al.*,[28] and even less with those reported by Edwards.[29,30]

The values reported by Edwards are very high relative to the others, even if one takes into account the differences in ionic strength used. However, if the results for other systems reported by Edwards in reference 30 are compared with other literature values, it will be noticed that his values are all considerably higher. When the formation curves obtained by Edwards are compared with those obtained in this work the former are seen to lie at lower free ligand concentrations, which implies greater stability of the complexes present. Thus there seems to be something inherent in the experimental method employed by Edwards that gives rise to higher values. His manner of calculating log K values by the 'half $\bar{n}$ method' may be the problem. The equilibria in this system are not sufficiently separated for this method

Table 3 Stability constants obtained for Ni (II) with etolen, together with the values reported in the literature. (All data are for 25°C.)

log K_{011}	log K_{012}	Medium	Reference
6.955(9)	5.83(1)	0.5 mol dm^{-3} KNO_3	This work (ESTA)
6.96(1)	5.82(2)	0.5 mol dm^{-3} KNO_3	This work (MINIQUAD)
6.97-0.3	5.83	0.5 mol dm^{-3}	26
6.97	5.83	0.5 mol dm^{-3} $NaC10_4$	27
6.66	5.80	0.5 mol dm^{-3} KNO_3	28
6.82	5.62	0.1 mol dm^{-3}	26
7.78	6.08	1 mol dm^{-3} KCl	29,30
6.76	5.52	0	26

to be reliable. As his 'raw' data were not available it was not possible to re-analyze his data to see if any improvement could be achieved.

Although the value reported by Hall *et al.*[28] for log K_{012} is in fair agreement with the values reported later, the value of log K_{011} is substantially lower. The reason for this discrepancy is not apparent. The work reported here, like that of other authors,[27,28,30] does not provide evidence for the formation of a $Ni(etolen)_3{}^{2+}$ complex in solution. Breckenridge[31] and Karpeiskaya *et al.*[32] report the formation of such a complex in the *solid* state, however. It has been shown [33] by means of n.m.r. contact shifts that etolen behaves as a terdentate ligand in aqueous solution. This seems to indicate that the ML_3 complex, which requires etolen to bind as a bidentate ligand, does not form in solution.

To calculate the heats of formation of the nickel-etolen complexes, LETAGROP KALLE was provided with the stability constants and enthalpy changes for the species H_2O, HL^+, H_2L^{2+} and Ni $(OH)^+$, and the stability constants for ML^{2+} and $ML_2{}^{2+}$. The thermodynamic parameters obtained for the formation of $Ni(etolen)^{2+}$ and $Ni(etolen)_2{}^{2+}$ are shown in Table 4, together with pertinent values reported in the literature.

The enthalpy changes obtained for the formation of the nickel-etolen complexes do not agree well with the values reported by Barbucci.[4] However, the calorimetric results obtained for the protonation experiments obtained with the same equipment[15] agree very well with those of Barbucci. This seems to indicate that the experimental methods used here are not in question. The discrepancy could arise from the way Barbucci performed the complex formation titrations. He destroyed the nickel-etolen complexes by addition of excess nitric acid. This indirect method has the disadvantage that the heat liberated by the reactions of interest is overshadowed by the heat liberated by protonation reactions. In this work the heat liberated was a direct measure of the extent of complex formation. The $p[H^+]$ in Barbucci's experiments would also have been higher than in the experiments reported here where part of the background electrolyte was replaced by protonated ligand. This higher $p[H^+]$ may have led to hydrolysis reactions which were not taken into account. Apart from the reasons mentioned above, it is difficult to explain the discrepancy, especially as the same model of species in solution and virtually the same stability constants were used in the calculations.

The exothermicity of the complex formation reactions is expected, because these are reactions between a fairly 'soft' ligand and a metal ion which is borderline[34] between 'hard' and 'soft'. Hence, the energy released to form the metal-nitrogen bonds greatly exceeds that required to displace the coordinated water

Table 4 Thermodynamic parameters of complex formation for Ni(II) with etolen. All data are for 25°C.

log K_{011}	ΔH^θ_{011}/ kJ mol^{-1}	ΔS^θ_{011}/ J mol^{-1} K^{-1}	log K_{012}	ΔH^θ_{012}/ kJ mol^{-1}	ΔS^θ_{012}/ J mol^{-1} K^{-1}	Medium	Reference
6.96	-29.7(2)	33.6	5.82	-37.8(4)	-15.4	0.5 mol dm^{-3} KNO_3	This work
6.97	-32.6(5)	24.3(1.7)	5.83	-34.8(1.0)	-5.0(3.3)	0.5 mol dm^{-3} $NaC10_4$	4

molecules. The greater exothermicity on reaction with a second ligand molecule is in keeping with the behaviour of many 3d metal ions when reacted with polyamines, and has been explained as follows.[35] On the addition of a molecule of ligand, the charge on the metal ion is partially neutralized and the soft character of the metal ion is enhanced. Thus the reaction with a second ligand molecule will involve a more covalent interaction, with a correspondingly greater (exothermic) heat of reaction.

The entropy change for the first step is positive and that for the second step is negative. This is in keeping with the model for metal-polyamine complex formation suggested by Paoletti *et al.*[35] They explain the observation as follows. On complex formation, solvent molecules attached to the metal ion and ligand are released, which makes a positive contribution to the entropy change. This positive contribution is partially offset by the loss of ligand entropy on formation of the chelate ring. However, for the first step of complex formation the former contribution is greater than the second and so the overall entropy change is positive. The addition of a ligand molecule to the metal ion causes a dielectric screening of the metal ion, which in turn results in a decrease in the interaction with the solvent. Hence , on addition of a second chelating ligand, fewer water molecules are released and the loss in ligand entropy exceeds the positive contribution made by the release of solvent molecules. This results in decreasing entropy changes with successive steps of complexation.

In considering the entropy change for the reaction $Ni^{2+} + 2L \rightleftharpoons NiL_2^{2+}$, Barbucci[4] used the fact that the value for etolen (19.2 J mol^{-1} K^{-1}) is larger than that for diethylenetriamine (dien) (0 J mol^{-1} K^{-1}) to suggest that one of the alcohol groups in $Ni(etolen)_2^{2+}$ is not coordinated to the metal ion. The value obtained here for the entropy change (18.2 J mol^{-1} K^{-1}) is only slightly smaller. One can however explain the entropy changes observed for the formation of the nickel-etolen complexes by making use of the results of Everhart *et al.*[33] They showed for $Ni(etolen)(H_2O)_3^{2+}$ that, although $\Delta H°$ for coordination of the alcoholic oxygen is zero, coordination of this donor atom is favoured by a gain in entropy of about 6.3 J mol^{-1} K^{-1}. When this result is used in conjunction with the entropy changes for the nickel-dien complexes in the equation

$$\Delta S°_{(pqr)}(etolen) = 2[\Delta S°_{(pqr)}(dien)/3] + 6.3$$

one obtains $\Delta S_{011}° = 30.0$ J mol^{-1} K^{-1} and $\Delta S_{012}° = -17.4$ J mol^{-1} K^{-1} for the stepwise formation of the nickel-etolen complexes. These estimates are fairly close to the experimentally observed values. It therefore seems reasonable to assume that etolen behaves as a terdentate ligand in these complexes.

The formation curves obtained from the potentiometric data for the nickel-oden system are shown in Figure 1. One notable feature is that the curve for titration no. 3 (denoted by x) lies slightly above the others. This titration was carried out at the lowest metal ion concentration used ($[Ni^{2+}]_0 = 5.007 \times 10^{-4}$ mol dm^{-3}). It is well known that titrations involving sub-millimolar concentration levels are more prone to experimental error, so it was concluded that this upward displacement was merely a reflection of slight inaccuracies in the solution concentrations.

Those titrations (nos. 1-3) which were carried out at higher $p[H^+]$ values exhibit 'back-fanning' effects. The $\overline{Z}_M$ function is known to be more sensitive to errors in the concentrations of the components at high $p[H^+]$ values than at low values, hence leading to the occurrence of sudden increases in the value of $\overline{Z}_M$, which are

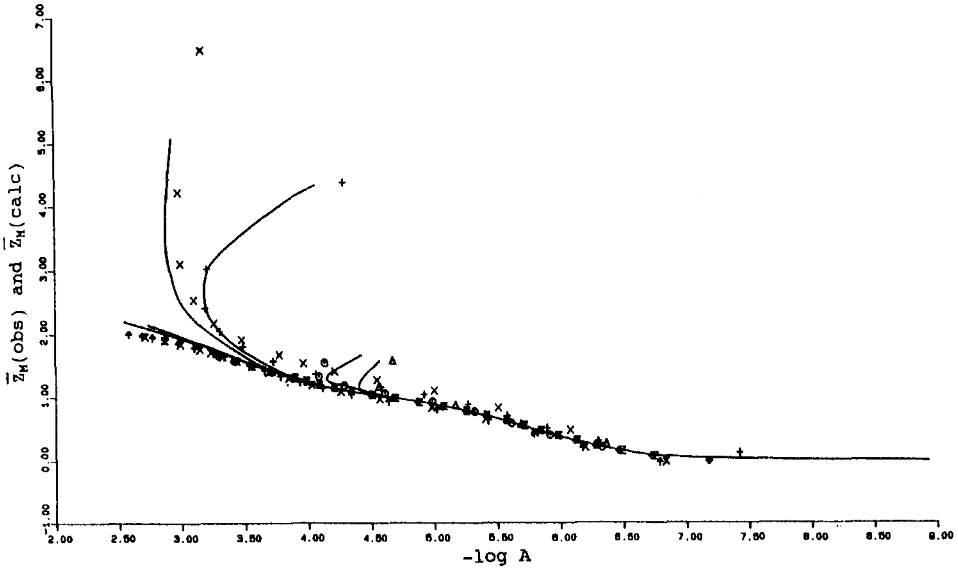

Figure 1 Formation curves for the nickel – oden system. In the plots of these curves the symbols ⦶, Δ, +, ×, ◇, ↑ and Ƶ are used, in that order, to represent the successive titrations.

sometimes observed after the plateau region. These findings are in keeping with those of Cabani[36] and Avdeef *et al.*[37] The reason why $\bar{Z}_M$ is not very sensitive to concentration errors at low values of p[H$^+$] is that in this region the total excess concentration of hydrogen ions, [H$^+$]$_t$, is always significantly larger than the concentration of free hydrogen ions, [H$^+$]. This results from the presence of substantial amounts of protonated ligand. The 'back-fanning' effects are however observed even for $\bar{Z}_M$ values somewhat less than 2. This suggests that these effects may not be due only to experimental error, and that the possible presence of hydrolysed or protonated species needs to be investigated. The 'back-fanning' feature starts at lower $\bar{Z}_M$ values for titration no. 1 than for the other two. This is not surprising, because no.1 was carried out at the highest metal to ligand ratio of the three. The operating p[H$^+$] was therefore higher and hydrolysis more likely to occur at an early stage. It is interesting to note that those titrations (nos. 4-7) which were carried out with protonated ligand as part of the background electrolyte exhibit no obvious hydrolysis and level off at $\bar{Z}_M$ = 2.

The plots of the repeat titrations (nos. 4 and 7) were completely superimposable, which indicates that the results are reproducible. The data gathered in the forward and reverse parts of titration no.1 are also superimposable, up to $\bar{Z}_M \sim$ 1. Thus, within experimental error, the formation curves are superimposable (apart from the 'back-fanning' features), and one can conclude that no polynuclear species are present.

For model selection purposes, ML and ML$_2$ were treated as the major complexes present. Attempts were then made to introduce various protonated and hydrolysed species into the model. Fixed values were used for the stability constants of the species H_2O, HL$^+$, H_2L^{2+} and Ni(OH)$^+$. Table 5 lists the results obtained for the

Table 5 Stability constants* for Ni(II)-oden complexes obtained from different models.

Model	1	2	3	4
ML^{2+}	5.86	5.75	5.75	5.78
ML_2^{2+}	9.91	9.30	9.20	9.25
$ML(OH)^+$			-3.60	-4.65
$ML_2(OH)^+$				-0.33
Titrations used	1-3	4-7	1-7	1-7
No. of points	44	83	127	127
U_{ESTA}	3124	81	635	369
R_{ESTA}	0.030	0.004	0.012	0.009

*For complexes containing the hydroxide ion, e.g. $ML_r(OH)p$, the values given in the table represent log β_{-p1r} + p(log K_w).

'successful' models tried, *i.e.*, those models for which the program ESTA yielded successful refinements.

For models 1 and 2 the data were divided into two sets. One set (titrations 4-7) consisted of those titrations which were carried out with protonated ligand as part of the background electrolyte, and exhibited no 'back-fanning'. The titrations in the other set (nos. 1-3) did not use protonated ligand, and did exhibit 'back-fanning'. All attempts to include hydroxy species in the model failed when the two sets were treated separately. The 'back-fanning' features could be reproduced only when the complete data set was used. On the basis of the value of the objective function U, model 4 was taken to be the best description of the species present in solution. It is pleasing to note that the stability constants in model 4 for the species ML and ML_2 are fairly close to those obtained in model 2. Calculated formation curves obtained from the stability constants used in model 2 exhibit all the features expected when only two mononuclear species are present in solution. The results obtained for model 4 are compared with literature values in Table 6.

The formation curves calculated by using the stability constants from model 4 are depicted in Figure 1. One can see that they reproduce the essential features of the observed formation curves. The agreement is very good except at $\bar{Z}_M$ values above 1.8. It is known, however, that the results are more sensitive to uncertainties in the solution concentrations for high $\bar{Z}_M$ values than low.

As can be seen from Table 6, the results obtained for log K_{011} and log K_{012} do not agree closely with any of the values previously reported, but they do lie well between the extremes of those values. It is possible that the values reported by Barbucci and Vacca[5] are higher because they did not consider the possibility that any species other than ML and ML_2 were present in solution. In their potentiometric titrations the p[H^+] values covered ranged from 3.0 to 11.2. This range is wider than that covered in this work (6.9 - 10.4). Thus the formation of hydroxy species in their experiments appears extremely likely. On the basis of model 4, one would expect to find hydroxy complexes in the work of Lotz *et al.*,[39] but such complexes are not reported there either.

There are no literature values available for comparison with the stability constants found for the ternary hydroxy complexes. The $ML(OH)^+$ complex has also been reported in the systems involving oden and Cu^{2+} or Zn^{2+}[5]. It is most likely that this complex is formed by the deprotonation of a coordinated water molecule.[35] The $ML_2(OH)^+$ complex is possibly formed by substitution of a hydroxide ion for one of the coordinated ligand donor atoms. In this case the atom

Table 6 Thermodynamic parameters of complex formation for Ni(II) with oden.

Reaction	log K	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}	Temperature/°C	Medium	Reference
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	5.78(1)	-29.1(2)	13.1	25	0.5 mol dm^{-3} KNO_3	This work
$NiL^{2+} + L \rightleftharpoons NiL_2{}^{2+}$	3.47(3)	-26.7(6)	-23.1	25		
$Ni^{2+} + L + OH^- \rightleftharpoons NiL(OH)^+$	9.1(3)†	—	—	25		
$Ni^{2+} + 2L + OH^- \rightleftharpoons NiL_2(OH)^+$	13.41(6)*	-36.69(4)	133.7	25		
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	5.895(5)	-28.0(8)	19(3)	25	0.5 mol dm^{-3} KNO_3	5
$NiL^{2+} + L \rightleftharpoons NiL_2{}^{2+}$	3.62(2)	-27(2)	-21(8)	25		
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	5.62	-29	8	25	0	38
$NiL^{2+} + L \rightleftharpoons NiL_2{}^{2+}$	3.39	-29	-33.5	25		
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	5.93(1)	-29.7	8	10	0_{corr}	39‡
	5.75(1)			20		
	5.54(1)			30		
	5.41(1)			40		
$NiL^{2+} + L \rightleftharpoons NiL_2{}^{2+}$	3.69(7)	-31.4	-42	10		
	3.50(6)		-42	20		
	3.19(6)		-42	30		
	3.18(6)		-38	40		

$^†\log\beta_{-111}$, $^*\log\beta_{-112}$, ‡In this case the numbers in parentheses represent 95% confidence limits could be either the primary nitrogen atom or the ethereal oxygen atom. The fact that hydroxy species were formed here but not in the nickel-etolen system is in keeping with the higher basicity of oden, and the precipitation encountered in the preliminary calorimetric experiments.

In order to visualize the relative amounts of ternary complexes present at some typical concentrations and metal to ligand ratios, two species distribution diagrams are shown in Figures 2 and 3. Figure 2 refers to a titration which used protonated ligand as part of the background electrolyte. At the highest p[H$^+$] reached in this titration, *viz*, 8.90, less than 11% of the total nickel is present as ternary species. Figure 3 refers to a titration in which protonated ligand was not present in the background electrolyte and for which the metal to ligand ratio was much lower. At the highest p[H$^+$] reached here, 10.39, about 90% of the total nickel is present as ternary species. From these examples it is clear that the substitution of part of the background electrolyte by protonated ligand leads to a marked decrease in the formation of hydrolysed species. The protonated ligand prevents the working p[H$^+$] from rising to too high a value near the end of the titration.

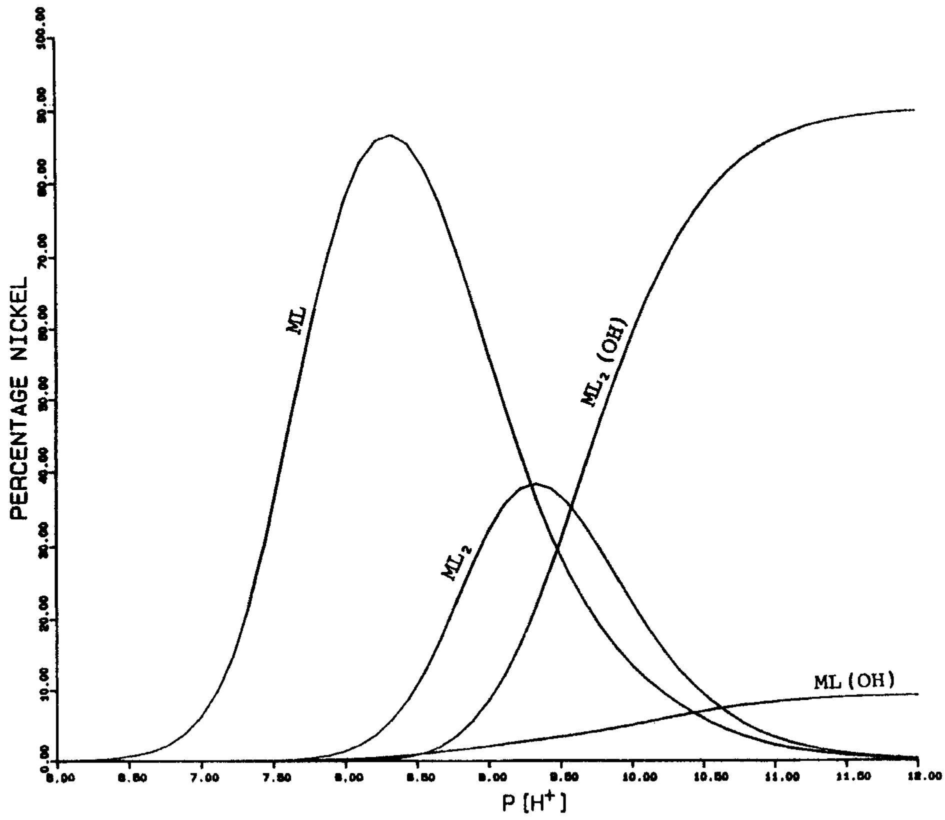

Figure 2 Species distribution diagram for the nickel - oden system, for the case $[Ni^{2+}]_t$ = 5.0×10^{-3} mol dm^{-3} and $[oden]_t/[Ni^{2+}]_t = 2.0$.

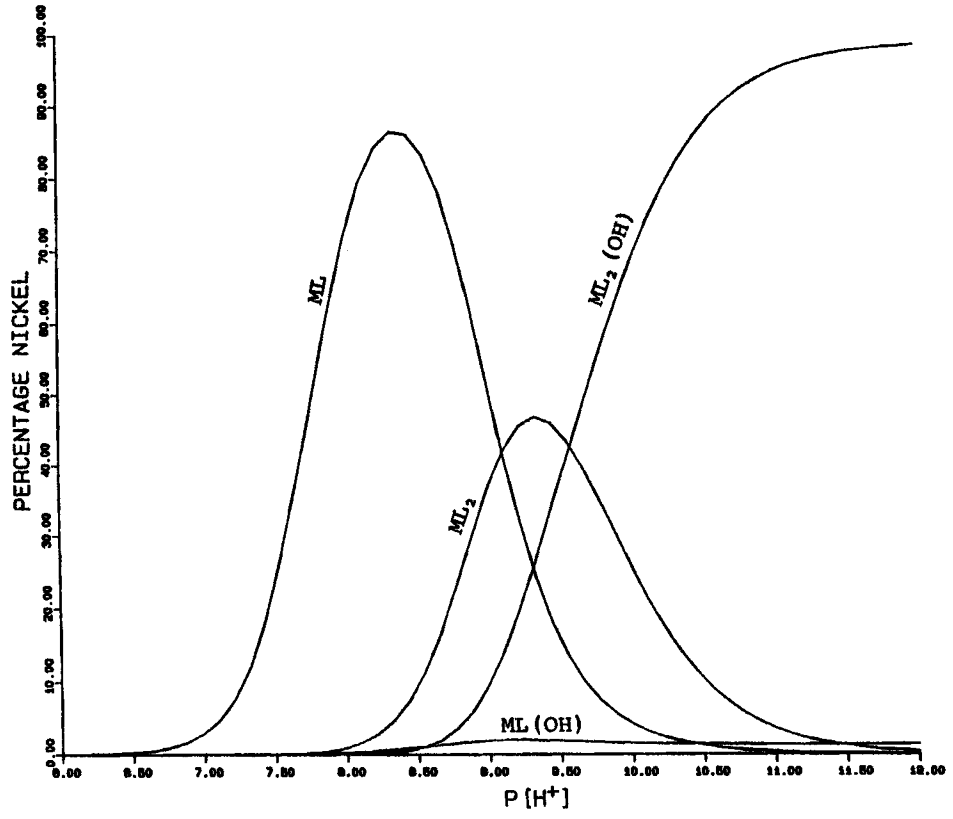

Figure 3 Species distribution diagram for the nickel - oden system, for the case $[Ni^{2+}]_t = 5.0 \times 10^{-4}$ mol dm^{-3} and $[oden]_t/[Ni^{2+}]_t = 9.0$.

In the calculation of the heats of formation of the nickel-oden complexes fixed values were used for the stability constants and enthalpy changes of the species H_2O, HL^+, H_2L^{2+} and Ni $(OH)^+$, and for the stability constants of ML^{2+}, ML_2^{2+}, $ML(OH)^+$ and $ML_2(OH)^+$. The results obtained are shown in Table 6, together with pertinent values reported in the literature. The enthalpy changes obtained for the ML and ML_2 complexes agree fairly well with the reported values. No reliable value of $\Delta H°$ could be determined for the formation of the $ML(OH)^+$ complex (species distribution calculations confirmed that no significant amount of $ML(OH)^+$ was formed during the calorimetric titrations).

The magnitude of $\Delta H°_{011}$ is greater than that of $\Delta H°_{012}$, which reverses the usual order for polyamines (*c.f.*, etolen). Barbucci and Vacca[5] suggested that the second ligand addition step is less exothermic for the following reason. The complex ML (where L is terdentate) may exist in solution as the *meridional* or the *facial* isomer. However, in the ML_2 complexes, the ligand are usually *equatorially* placed and a certain amount of *facial*→*meridional* conversion therefore takes place during the second ligand addition step. It was found by Evilia *et al.*[40] that this conversion is endothermic in the case of Ni^{2+} and oden. Hence this conversion decreases the value of ΔH°_{012}.

The above explanation presupposes that the ML_2 complex is *meridional.* This assumption is justified by Barbucci and Vacca on the grounds that the rather similar $Ni(dien)_2{}^{2+}$ complex is *meridional* in the solid state. There is however no evidence to suggest that the stereochemistry observed in the solid state is maintained in solution. In fact there are suggestions to the contrary.[35] The crystal structure of $Ni(oden)_2{}^{2+}$ has not yet been reported.

This decrease in the enthalpy change on addition of a second ligand molecule was also observed in studies of the ligand dipropylenetriamine (dpt) with Ni^{2+}, where it was known that all the nitrogens are coordinated to the metal ion in solution.[41] In that case steric repulsion between the two ligand molecules was used to account for the phenomenon. This may also be the explanation in the case of oden. Another possible explanation is that in the second step of complexation more water molecules are displaced. This endothermic effect lowers the heat liberated in spite of the fact that the second step involves a softer interaction and should be more exothermic than the first. If this increased desolvation effect were operative it would manifest itself in abnormally large ΔS° values. As this does not obviously occur, the previous explanation is the more plausible of the two. Again, the entropy changes observed follow the usual trend for polyamines.

A comparison of the stability constants obtained for etolen and oden complexes of Ni(II) shows that the oden complexes are weaker than those of etolen. This is in keeping with the supposition that the stability of a nickel-polyamine complex increases as the number of secondary nitrogen donors increases at the expense of primary nitrogen donors.[1] On the other hand, Barbucci and Vacca[5] and Lotz *et al.*[39] ascribed this lower stability of the oden complexes to the destabilizing effect of the ether oxygen. This lower stability cannot be ascribed to non-coordination of the ether oxygen, because it has been shown that in aqueous solution oden behaves as a terdentate ligand towards Ni^{2+}.[40] The lower stability of oden complexes is also due to a somewhat less favourable enthalpic contribution. The smaller positive entropy change observed for the formation of the ML^{2+} complex involving oden suggests differing degrees of solvation of the ML^{2+} complexes of the two ligands. The difference between the $\Delta S^\circ{}_{011}$ values for the nickel complexes of etolen and oden (20.5 J mol^{-1} K^{-1}) suggests that in the reaction with oden at least one water molecule fewer is liberated (liberation of one water molecule corresponds to an increase in translational entropy of at least 21 J mol^{-1} K^{-1}).[35] If this is so, then it would be in keeping with the findings of Evilia *et al.*[40] that at 300 K $Ni(oden)^{2+}$ is found to exist primarily as the *facial* species, and that this geometry may be stabilized by coordinated water molecules. The presence of these coordinated water molecules may sterically hinder the attachment of the second ligand molecule and thus give rise to the unexpected lower value of ΔH°_{012}.

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