Potentiometric and Spectrophotometric Study of the Solution Equilibria in the Nickel(II)–Diethanolamine–Water System in Aqueous Sodium Perchlorate Solutions at 25 °C

Aritz Lopategi, Rosario Castaño, Nestor Etxebarria and Juan M. Madariaga
Kimika Analitikoaren Saila, Euskal Herriko Unibertsitatea (UPV/EHU), P. K. 644, E-48080 Bilbao, Spain

The acid–base and complexation equilibria of the system nickel(II)–diethanolamine–water have been studied using an automated potentiometric–spectrophotometric titration system at 25 °C and at four ionic strengths (0.5, 1.0, 2.0 and 3.0 mol dm^{-3}) in $NaClO_4$ medium. The stoichiometric stability constants, obtained at the different ionic strengths, were correlated by means of the modified Bromley methodology and the corresponding thermodynamic constants were: log $^{\circ}\beta_{011}$ = 8.88 ± 0.02, log $^{\circ}\beta_{110}$ = 2.67 ± 0.02 and log $^{\circ}\beta_{120}$ = 4.42 ± 0.05.

Many industrial processes dealing with the management of wastes and many of the treatments used to reduce the stress on the environment are still based on destruction of the wastes.[1,2] Whereas environmental concerns have resulted in many improvements in the technical processes, the scarcity of some raw materials (metals, water, *etc.*) together with the application of more restrictive policies have impelled the development of recycling and reuse technologies, raising the added value of the manufactured goods.[3]

Some of the industrial processes which produce wastes containing organic solvents, mineral acids, organic and inorganic compounds and metallic wastes are metal electroplating and finishing. Among the different metals and excluding the precious ones, nickel has the highest added value and it is estimated that only 10% of the annual consumption is recycled.[3] Among the organic compounds usually found in electrolytic nickel baths, carboxylic acids (citric, tartaric and oxalic), substituted amines (mono-, di-, tri-ethanolamines), surfactants and polyaminocarboxylic acids are the most common.[1,2] The most common treatment of waste waters containing nickel is the precipitation of nickel hydroxide, followed by pouring off and filtration, but it has been experimentally observed that the presence of some of the above-mentioned organic compounds can result in incomplete precipitation of the metal due to the formation of complexes in solution.[4] Such discrepancies between actual and predicted behaviour of samples make it necessary to elaborate new methods to eliminate and recover the metal from wastes.

The modelling of the behaviour of different chemical systems can be of great advantage in the development of new 'clean' technologies and in the study of the species distribution in order to improve the control systems of industrial processes. A chemical model based on thermodynamic grounds is required and, thus, it is necessary to know the nature of the different species formed under certain conditions and how they are affected by the temperature, pressure, ionic strength and the concentration of the components. Such studies have been made for natural aqueous systems[5–7] where the amount of chemical components is not very large and the equilibria involved are fairly well known.[6,7] Nevertheless the modelling of industrial wastes has not been studied as extensively due to the many different chemicals and equilibria involved.[8]

The system nickel(II)-diethanolamine (dea)-water was considered suitable to build a chemical model that can be employed to interpret the general behaviour of this kind of organic compound in the nickel plating processes. There was not enough information about the acid–base and complexation equilibria of the dea-water and nickel(II)-dea-water systems in order to build a thermodynamic model including the variation of the stability constants with ionic strength. Thus, in this work a systematic potentiometric and spectrophotometric study of the nickel(II)–diethanolamine–water system has been performed at four different ionic strengths using $NaClO_4$ as the inert electrolyte. The constants obtained together with literature values have been correlated with the ionic strength by means of the modified Bromley methodology.[9,10]

Experimental

Reagents and Solutions.—All reagents were used without further purification. Sodium perchlorate monohydrate (Fluka p.a.) was employed as ionic medium and the concentration of the stock solution was tested gravimetrically after evaporation of different aliquots at 110 °C. The concentration of the stock solution of diethanolamine (Merck p.a.) was checked acidimetrically with perchloric acid employing potentiometric techniques to determine the equivalence point.[11] A stock solution of nickel(II) perchlorate was made from nickel(II) perchlorate hexahydrate (Merck p.a.) and its concentration was determined by complexometric titration with ethylenediamine-*N,N,N',N'*-tetraacetate and murexide as indicator.[11] Stock solutions of perchloric acid (Fluka p.a.) and sodium hydroxide (Merck p.a.) were standardized against tris(hydroxymethyl)aminomethane and potassium hydrogenphthalate (both Merck p.a.) respectively.[11]

Apparatus.—The experiments were carried out by means of an automatic potentiometric–spectrophotometric titration system developed in our laboratory[12] which can control up to three titrations at the same time. The potentiometric measurements were made with the cell in Scheme 1 where I is the ionic strength of the solution. The glass electrode (Metrohm 6.0101.100) and the double liquid-junction reference electrode [Ag–AgCl (s), Metrohm 6–0726–100-RC] were connected to a preamplifier in order to adapt the electrical signal to a Hewlett-Packard HP 3421A voltmeter connected to a computer. A UV/VIS diode-array Hewlett-Packard HP8452A spectrophotometer was also connected to the computer by means of an IEEE-488 (HP-IB) interface. The titrated solution was introduced to the spectrophotometric cells (Hellma 104F-QS, path length = 1 cm) with a Gilson Minipuls 2 pump at the rate of 2 cm^3 min^{-1}. The inlet solution was filtered to avoid precipitation inside the tubing. The titrant additions were performed with a MicroBu 2031 CRISON automatic burette

Ag–AgCl(s)	I mol dm^{-3} NaClO$_4$ AgCl (sat)	I mol dm^{-3} NaClO$_4$	Test solution	Glass electrode

Scheme 1

Table 1 Values of log k_w and the liquid-junction coefficient at different ionic strengths in NaClO$_4$ medium

I/mol dm^{-3}	log k_w	j_{ac}/mV dm^3 mol^{-1}	j_{ba}/mV dm^3 mol^{-1}
0.5	− 13.69 ± 0.01	− 103 ± 2	140 ± 1
1.0	− 13.75 ± 0.01	− 71 ± 2	92 ± 2
2.0	− 13.94 ± 0.01	− 37 ± 2	50 ± 1
3.0	− 14.12 ± 0.01	− 17 ± 2	69 ± 1

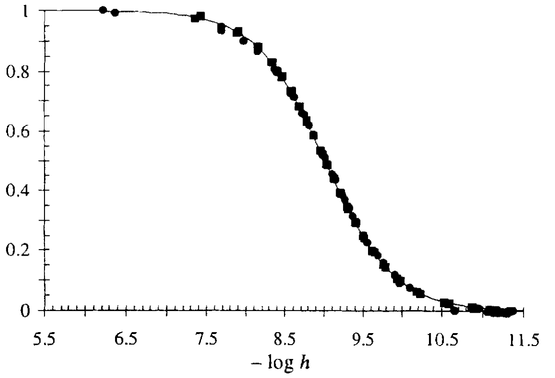

Fig. 1 Plot of the Z function *versus* $-\log h$ at 0.5 mol dm^{-3} NaClO$_4$ ionic strength and different diethanolamine concentrations; c_{dea} = 0.014, (●) and 0.028 mol dm^{-3} (■); (—) theoretical curve

with a minimum reading of 0.002 cm^3. The titrations were made at 25 ± 0.1 °C in a thermostatted oil-bath and CO$_2$ was removed by bubbling N$_2$ through the solution. Magnetic stirring was employed during the titration.

Procedure.—Two different kinds of titrations were performed. In order to calculate the protonation equilibrium constant of diethanolamine potentiometric titrations were carried out. An aliquot (75–80 cm^3) of a solution containing dea (10^{-2}–3×10^{-2} mol dm^{-3}) and the necessary amount of NaClO$_4$ stock solution to keep the ionic strength constant were titrated with a (Na$^+$, H$^+$)ClO$_4^-$ solution at the same ionic strength. At the beginning of each titration an excess of NaOH was added to calculate the standard potential ($E°$) of the electrolytic cell in Scheme 1. In this case, it was considered that equilibrium was reached when the standard deviation of the last three potential measurements was $\leqslant \pm 0.05$ mV.

In order to establish the nature of the complexation equilibria in the system nickel(II)–dea–water both potentiometric and spectrophotometric titrations were made. An aliquot (75–80 cm^3) of a solution containing Ni^{2+} and dea at different metal : ligand ratios (1 : 10–1 : 36) and the necessary amount of NaClO$_4$ to keep the ionic strength constant was titrated with an Na$^+$ (OH$^-$, ClO$_4^-$) solution at the same ionic strength. In order to calculate the $E°$ value an excess of HClO$_4$ was added and the titration was carried out until a solid phase was observed. The nickel concentration employed was fairly large (10^{-2}–3×10^{-2} mol dm^{-3}) due to the low value of the molar absorption coefficient of Ni^{2+}. The spectrophotometric measurements were made in the wavelength range 350–800 nm every 2 nm. It was considered that equilibrium was reached when both criteria σ_E (standard deviation of electromotive force) $\leqslant \pm 0.05$ mV and σ_A (standard deviation of absorbance) $\leqslant \pm 0.002$ were obeyed.

The ionic strengths studied were 0.5, 1.0, 2.0 and 3.0 mol dm^{-3} and at least four titrations were made at each and for each type of titration.

Other Measurements.—Two different experimental quantities were measured, the free hydrogen-ion concentration and the absorbance of the solution.

Making use of the Nernst equation[13] the free hydrogen-ion concentration (h) can be calculated from equations (1) and (2).

$$E = E° + g \log h + E_j h \qquad (1)$$

$$E_j h = j_{ac} h + j_{ba} k_w h^{-1} \qquad (2)$$

As can be seen, it is necessary to know the values of k_w (water autoprotolysis constant) and the acid (j_{ac}) and base (j_{ba}) liquid-junction potential coefficients (mV dm^3 mol^{-1}), which were evaluated previously by means of ionic medium titrations, in order to determine h. First Gran's method[14] was used and later the values (k_w, j_{ac} and j_{ba}) were numerically refined by means of the MODEL FUNCTION version[15] of the LETAGROP program.[16] The values obtained at the different ionic strengths are collected in Table 1. As their values depend only on the ionic strength[13] they can be considered constants in the ligand and metal–ligand potentiometric titrations, while the value of the standard potential ($E°$) may change from day to day and it is necessary to evaluate it in each titration.

On the other hand the absorbance of the solution can be related with the species present by means of the Lambert–Beer law, equation (3) where A_{exptl} is the experimental absorbance, b is the path length of the spectrophotometric cell, ε the molar absorption coefficient and c the concentration of the species which contribute to the absorbance of the solution. The subscripts i and j indicate the different wavelengths and the different species contributing respectively. On combining equation (3) with the mass balance equations and the value of

$$A_{exptl,\lambda_i} = b \sum_{j=1}^{N} \varepsilon_{i,j} c_j \qquad (3)$$

(h) calculated previously, it is possible to explain the absorbance changes in terms of the formation of new species and to calculate the values of their stability constants as well as their molar absorption coefficients.

Calculations and Results

Diethanolamine Acid–Base Equilibrium.—The acid–base equilibria of diethanolamine can be written as in equation (4)

$$\mathrm{dea} + r\,\mathrm{H}^+ \rightleftharpoons \mathrm{H}_r\mathrm{dea}^{r+} \qquad (4)$$

where dea is the neutral diethanolamine molecule. The protonation constant for a given medium of constant ionic strength can be expressed as in equation (5) where the

$$^{I}\beta_{1r} = [\mathrm{H}_r\mathrm{dea}^{r+}]/[\mathrm{dea}][\mathrm{H}^+]^r \qquad (5)$$

superscript I indicates the ionic strength. To a first approximation the stoichiometry and the values of the formation constants were graphically evaluated by means of the Z function,[13] which can be defined as the average number of ligands bound to a central ion. In this case, Z can be expressed as in equation (6) where $[\mathrm{H}]_{tot}$ and c_{dea} are the total

$$Z = \frac{[\mathrm{H}]_{\mathrm{tot}} - h + [\mathrm{OH}]_{\mathrm{f}}}{c_{\mathrm{dea}}} = \frac{\Sigma r\beta_{1r}h^r}{1 + \Sigma\beta_{1r}h^r} \qquad (6)$$

concentrations of protons and diethanolamine respectively and h and $[\mathrm{OH}]_{\mathrm{f}}$ denote the free concentrations of protons and hydroxide ions respectively. As it can be seen in Fig. 1, the Z function is independent of the total concentration of dea which confirms the assumption that only mononuclear species involving dea are formed.

On the other hand in the range pH 5.5–11.5 the Z values are between 1 and 0 which suggests that there is only one protonation step. Thus, in order to calculate the protonation constant of dea, the classical treatment of the Z function using the normalized variable $U = {}^{\prime}\beta_{11}h$ was applied. The experimental curves Z *vs.* $-\log h$ and the theoretical curve Z *vs.* $-\log U$ were compared and from the position of the best fit it is possible calculate the value of the protonation constant of diethanolamine. The good agreement between the experimental Z curves for different total concentrations of dea and the theoretical curve plotted with the protonation constant proposed at $I = 0.5$ mol dm^{-3} $\mathrm{NaClO_4}$ is shown in Fig. 1.

The values of the protonation constants obtained graphically were refined numerically by means of the numerical programs BSTAC[17] and the NYTIT version of LETAGROP.[16] The BSTAC program minimizes the absolute sum of the square of the potential while NYTIT minimizes the absolute sum of the total hydrogen-ion concentrations. These programs not only allow refinement of the formation constant but also possible systematic errors in the analytical concentrations can be evaluated. The proposed protonation constants at each of the ionic strengths studied are listed in Table 2.

Nickel(II)*-Diethanolamine–Water System.—Complexation equilibria.* The complexation equilibria between nickel(II), diethanolamine and water can be described in a general way by means of equation (7), and the corresponding stoichiometric stability constants can be written as in (8).

$$p\,\mathrm{Ni}^{2+} + q\,\mathrm{dea} + r\,\mathrm{H}^+ \rightleftharpoons [\mathrm{Ni}_p(\mathrm{dea})_q\mathrm{H}_r]^{(2p+r)+} \qquad (7)$$

$${}^{\prime}\beta_{pqr} = \frac{[\mathrm{Ni}_p(\mathrm{dea})_q\mathrm{H}_r{}^{(2p+r)+}]}{[\mathrm{Ni}^{2+}]^p[\mathrm{dea}]^q[\mathrm{H}^+]^r} \qquad (8)$$

In order to establish the stoichiometry and the values of the stability constants of the possible complexes, it is necessary to know all equilibria which take place in the dea–water and nickel(II)–water systems. The first system has been described above, while Baes and Mesmer[18] provided a compilation and a critical study of nickel hydrolysis. At the total nickel concentrations employed in this work only the formation of the solid phase $\mathrm{Ni(OH)_2(s)}$ has been considered since other hydroxo complexes can be neglected.

(*i*) *Spectrophotometric studies.* Fig. 2 shows the absorption spectra for a metal:ligand ratio 1:10 in 3.0 mol dm^{-3} $\mathrm{NaClO_4}$ medium at different pH values. It can be seen that the absorbance increases with pH, whereas all maxima are displaced towards shorter wavelengths.

From these plots no conclusions about reactions occurring in the system or the composition of the species formed can be drawn. These can be deduced only after the data treatment which was made only numerically by means of the SPECFIT program[19] due to the great amount of data and the difficulty of handling them. A total of 26 wavelengths (from 350 to 760 nm every 16 nm) were treated. In all cases, the evolving factor analysis (EFA) showed a total of three principal components which could be related to three absorbing species: Ni^{2+}, $[\mathrm{Ni(dea)}]^{2+}$ and $[\mathrm{Ni(dea)_2}]^{2+}$. This model-free analysis of data was in very good agreement with the results obtained by means of the mass-balance-equations resolution algorithm.

Table 2 Stoichiometric stability constants for the nickel(II)–diethanolamine–water system at different ionic strengths in $\mathrm{NaClO_4}$ medium

I/mol dm^{-3}	$\log {}^{\prime}\beta_{011}$	$\log {}^{\prime}\beta_{110}$	$\log {}^{\prime}\beta_{120}$
0.5	9.01 ± 0.01	2.69 ± 0.02	4.43 ± 0.04
1.0	9.14 ± 0.01	2.78 ± 0.02	4.61 ± 0.02
2.0	9.43 ± 0.01	3.05 ± 0.02	5.03 ± 0.03
3.0	9.72 ± 0.01	3.27 ± 0.02	5.55 ± 0.02

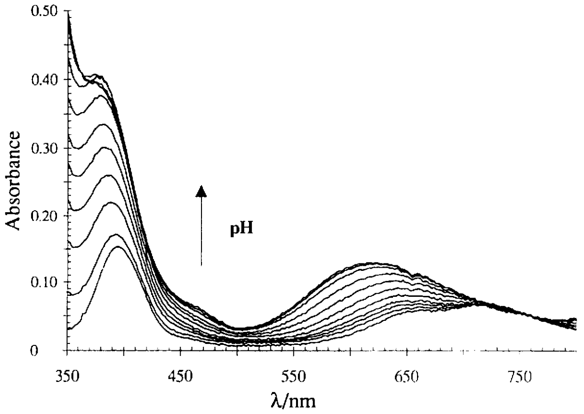

Fig. 2 Absorption spectra at different pH values of nickel(II)–diethanolamine solutions at 3.0 mol dm^{-3} $\mathrm{NaClO_4}$ ionic strength and metal:ligand ratio 1:10

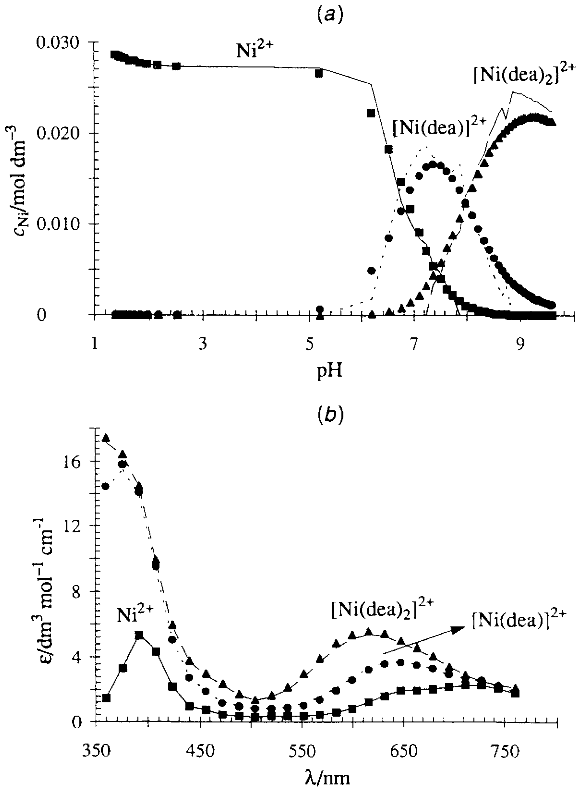

Fig. 3 (*a*) Concentration diagram of all species proposed by the model-free analysis of data (EFA) (lines) and calculated by the least-squares method (points) at a metal:ligand ratio of 1:10 and 3.0 mol dm^{-3} $\mathrm{NaClO_4}$ ionic strength. (*b*) Molar absorption coefficients of all species proposed by the EFA (lines) and calculated by the least-squares method (points)

However, due to some experimental difficulties, *e.g.* in some cases a displacement of the baseline during the titration, the spectrophotometric data have been employed only in a qualitative way to propose a chemical model and not in a quantitative way to calculate the equilibrium constants of the species formed.

Fig. 3(*a*) and 3(*b*) show the concentration diagram and the molar absorption coefficient for the system nickel(II)–dea–water at 3 mol dm^{-3} NaClO$_4$ ionic strength. The results obtained with both models (EFA and mass-balance-equations) are very close to each other. The squares correspond to the hexaaquanickel ion $[Ni(H_2O)_6]^{2+}$,[20] while the circles and the triangles correspond to $[Ni(dea)]^{2+}$ and $[Ni(dea)_2]^{2+}$ respectively. The second absorption maximum is displaced to shorter wavelengths, which explains the change in colour (from green to deep blue for high metal : ligand ratios) experimentally observed in the titrations.

(*ii*) *Potentiometric studies.* Graphical and numerical methods have also been employed to confirm the stoichiometries of the proposed species and their calculated stability constants.

The graphical treatment is based on the calculation of the Z values using the competitive-reactions method.[13] In this case the average number of dea molecules bound to nickel can be expressed as in equation (9) where $[dea]_f$ denotes the free

$$Z = \frac{c_{dea} - [dea]_f - [Hdea]}{c_{Ni}} \qquad (9)$$

diethanolamine concentration, [Hdea] the monoprotonated diethanolamine concentration and c_{dea} and c_{Ni} the total concentrations of diethanolamine and nickel respectively. It is possible to define $\bar{j}$ (the average number of protons bound to each diethanolamine molecule not bound to nickel) as in equation (10) where $c_{dea} - Zc_{ni}$ is the concentration of

$$\bar{j} = \frac{[H]_{tot} - h + [OH]_f}{c_{dea} - Zc_{Ni}} = \frac{\beta_{011}h}{1 + \beta_{011}h} \qquad (10)$$

diethanolamine not bound to nickel. As the value of β_{011} is known and h values can be determined from the potentiometric measurements it is possible to calculate $\bar{j}$ for each point of the titration.

Combining equations (9) and (10), expression (11) can be

$$Z = \frac{c_{dea}([H]_{tot} - h + [OH]_f)/\bar{j}}{c_{Ni}} = \frac{c_{dea} - ([dea]_f + \beta_{011}[dea]_f h)}{c_{Ni}} \qquad (11)$$

obtained where Z can be calculated from the first term of the equality and the free diethanolamine concentration, from the second one.

The formation curves for 3.0 mol dm^{-3} NaClO$_4$ ionic strength are given in Fig. 4. It can be seen that the Z values are independent of the total nickel concentration which indicates that no polynuclear species of nickel are formed. On the other hand, Z ranges from 0 and 1.6, so at least complexes with $q = 1$ and 2 can be considered, as was also concluded from the spectrophotometric results. It was not possible to obtain Z values above 2 due to the presence of a solid phase at pH > 9.5.

Thus, the classical treatment of the Z function was extended to a normalized variable $U = \beta_{110}[dea]_f$ and one-parameter $r = \beta_{120}/\beta_{110}{}^2$ treatment. In this way the Z function can be rewritten as in equation (12). From the position of the best fit

$$Z = \frac{\beta_{110}[dea]_f + 2\beta_{120}[dea]_f{}^2}{1 + \beta_{110}[dea]_f + \beta_{120}[dea]_f{}^2} = \frac{U + 2rU^2}{1 + U + rU^2} \qquad (12)$$

between the experimental and the theoretical curves the values of the stoichiometric stability constants are calculated at each of the four ionic strengths studied.

The results obtained graphically were refined by the numerical treatment. Although other chemical models were tried, the best was that proposed graphically. The programs employed were BSTAC[17] and the NYTIT version of LETAGROP.[16] In this case the results obtained with both programs were not comparable as far as NYTIT did not allow all titrations to be treated together. As with the diethanolamine protonation equilibria, these programs permitted evaluation of possible systematic errors.

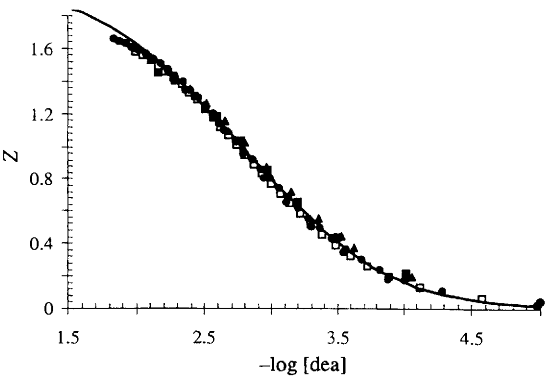

Fig. 4 Plot of the Z function *versus* $-\log$ [dea] at 3.0 mol dm^{-3} NaClO$_4$ ionic strength and different total nickel and diethanolamine concentrations: c_{Ni} = 0.01–0.03 mol dm^{-3}, c_{dea} = 0.2–0.36 mol dm^{-3}. Metal : ligand ratios: 1 : 36 (▲), 1 : 20 (■), 1 : 12 (□) and 1 : 10 (●); (—) theoretical curve

The proposed stability constants at the different ionic strengths studied are listed in Table 2.

Discussion

In order to construct a suitable thermodynamic model it is an advantage to have as many stoichiometric stability constant values at different ionic strengths and ionic media as possible. Several works on the diethanolamine acid–base equilibrium are available.[21–26] Most propose protonation constant values at only one ionic strength and in differ in the ionic media, so there is not enough experimental information to correlate these data. Only Oscarson *et al.*[26] have studied the protonation equilibrium of diethanolamine in KCl medium at six different ionic strengths and their values together with those proposed in this work in NaClO$_4$ medium have been employed to calculate the thermodynamic protonation constant of diethanolamine.

For the system nickel(II)–diethanolamine–water several literature references have been found[27–29] but either the stability constants were calculated at temperatures other than 25 °C or only one or two ionic strengths were studied. Thus only the values proposed in this work were employed in the calculation of the thermodynamic constants.

In this work the theory employed to construct the thermodynamic model was that of Bromley[9,10] which has been successfully applied to explain the hydrolysis of Nb^{V} and Ta^{V}[30,31] and the protolytic equilibria of 4-methylpyridine[32] and tartaric acid.[33]

In general, the different equilibria taking place in the nickel(II)–diethanolamine–water system can be described by equation (7) and their thermodynamic stability constants can be written as in (13) where $°\beta_{pqr}$ is the thermodynamic stability

$$°\beta_{pqr} = \frac{\{Ni_p(dea)_qH_r{}^{(2p+r)+}\}}{\{Ni^{2+}\}^p\{dea\}^q\{H^+\}^r} = \frac{[Ni_p(dea)_qH_r{}^{(2p+r)+}]\gamma_{Ni_p(dea)_qH_r{}^{(2p+r)+}}}{[Ni^{2+}]^p[dea]^q[H^+]^r\gamma_{Ni^{2+}}{}^p\gamma_{dea}{}^q\gamma_{H^+}{}^r} \qquad (13)$$

constant and γ denotes the molar activity coefficient ({ } indicates activity). Combining equations (8) and (13) gives expression (14) correlating the stoichiometric stability constants.

$$\log {}^{I}\beta_{pqr} = \log {}^{\circ}\beta_{pqr} + p \log \gamma_{\mathrm{Ni}^{2+}} + q \log \gamma_{\mathrm{dea}} + r \log \gamma_{\mathrm{H}^{+}} - \log \gamma_{\mathrm{Ni}_p(\mathrm{dea})_q\mathrm{H}_r{}^{(2p+r)+}} \quad (14)$$

The individual activity coefficients, on the molar scale, of charged species can be calculated using Bromley's equation (15)

$$\log \gamma_{\mathrm{M}} = -\frac{A Z_{\mathrm{M}}{}^{2} I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \sum_{x} \dot{B}_{\mathrm{MX}}(|Z_{\mathrm{M}}| + |Z_{\mathrm{X}}|)^{2} \frac{c_{\mathrm{X}}}{4} \quad (15)$$

where $A = 0.511$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$, I is the ionic strength on the molar scale, Z_{M} the charge of the M ion, Z_{X} that of the ionic species with opposite sign to M and c_{X} its molarity. The parameter $\dot{B}_{\mathrm{MX}}$ can be expressed as in equation (16) where B_{MX} is the interaction

$$\dot{B}_{\mathrm{MX}} = \frac{(0.06 + 0.6B_{\mathrm{MX}})|Z_{\mathrm{M}}Z_{\mathrm{X}}|}{[1 + (1.5/|Z_{\mathrm{M}}Z_{\mathrm{X}}|)I]^{2}} + B_{\mathrm{MX}} \quad (16)$$

parameter proposed by Bromley for the ion pair MX on the molar scale (dm^3 mol^{-1}).

In the case of uncharged species, such as the diethanolamine molecule, the activity coefficient can be calculated by means of Long–McDevit theory,[34] equation (17) where $S_{\mathrm{MX,\ ionic\ medium}}$ is

$$\log \gamma_{\mathrm{MX}} = S_{\mathrm{MX,ionic\ medium}}\, c_{\mathrm{ionic\ medium}} \quad (17)$$

the salt coefficient in the molar scale (dm^3 mol^{-1}) of a neutral species MX.

Combining equations (14)–(17) it is possible to obtain expression (18) ($\mathrm{X} = \mathrm{ClO_4}^-$ or Cl^-, $p = 0$) for the protonation equilibrium and (19) for the complexation equilibria ($r =$ 0) to correlate the stoichiometric stability constants at different ionic strengths in which the $\dot{B}$ functions are the corresponding Bromley's terms described in equation (16). Equations (18) and (19) depend only on the values of the thermodynamic stability constants and the interaction parameters (B) and the salt coefficient (S) of the species present in solution.

$$\log {}^{I}\beta_{011} = \log {}^{\circ}\beta_{011} + (\dot{B}_{\mathrm{H}^{+},\mathrm{X}^{-}} + S_{\mathrm{dea,ionic\ medium}} - \dot{B}_{\mathrm{Hdea}^{+},\mathrm{X}^{-}})I \quad (18)$$

$$\log {}^{I}\beta_{1q0} = \log {}^{\circ}\beta_{1q0} + \left(\frac{9\dot{B}_{\mathrm{Ni}^{2+},\mathrm{ClO_4}^{-}}}{4} + qS_{\mathrm{dea,NaClO_4}} - \frac{9\dot{B}_{\mathrm{Nidea_q}{}^{2+},\mathrm{ClO_4}^{-}}}{4}\right)I \quad (19)$$

The values of $B_{\mathrm{H}^{+},\mathrm{ClO_4}^{-}}$, $B_{\mathrm{H}^{+},\mathrm{Cl}^{-}}$, and $B_{\mathrm{Ni}^{2+},\mathrm{ClO_4}^{-}}$ were previously determined making use of (m, $\gamma_{\pm}$) literature values,[10] while the thermodynamic stability constants and the rest of the parameters have to be calculated. The correlation was made by means of the spreadsheet EXCEL 4.0[35] and the MODEL FUNCTION version[15] of LETAGROP.[16] Table 3 collects the results obtained for the different correlations. The thermodynamic protonation constant proposed in this work ($\log {}^{\circ}\beta_{011} = 8.89 \pm 0.02$) is in good agreement with that proposed by Oscarson *et al.*[26] from their data in KCl and by Bower *et al.*,[25] while no literature values for the thermodynamic constants of complexation equilibria were found.

Figs. 5 and 6 show the fit between the experimental values and the theoretical functions. The dependence of the stoichiometric stability constants on the ionic strength is almost linear due to the annulment of the first term in the activity coefficient expressions.

Both techniques employed in this work conclude that the best model to explain the experimental data is the formation of the complexes $[\mathrm{Ni(dea)}]^{2+}$ and $[\mathrm{Ni(dea)_2}]^{2+}$. On the other hand, the absorption spectra calculated with the SPECFIT program are in good agreement with those proposed by Bhat and Subrahmanya although these authors proposed three nickel–diethanolamine complexes, $[\mathrm{Ni(dea)}]^{2+}$, $[\mathrm{Ni(dea)_2}]^{2+}$ and $[\mathrm{Ni(dea)_3}]^{2+}$. This fact can be attributed to the much larger concentrations of diethanolamine employed in that study. Bjerrum and Djurdjevic[28] have discussed the low tendency of $[\mathrm{Ni(dea)_2}]^{2+}$ to take up further diethanolamine molecules in similar terms.

Table 3 Thermodynamic stability constants and interaction parameters obtained for the system nickel(II)–diethanolamine–water

Species[a]	$\log {}^{\circ}\beta_{pqr}$	$B_{pqr,\mathrm{ClO_4}^-}$
011[b]	8.88 ± 0.02	0.44 ± 0.01
110	2.67 ± 0.02	0.32 ± 0.04
120	4.42 ± 0.05	0.47 ± 0.04

[a] For species 010, $S_{pqr,\mathrm{NaClO_4}} = 0.54 \pm 0.01$ and $S_{pqr,\mathrm{KCl}} = -0.04 \pm 0.01$. [b] $B_{pqr,\mathrm{Cl}^-} = -0.12 \pm 0.01$.

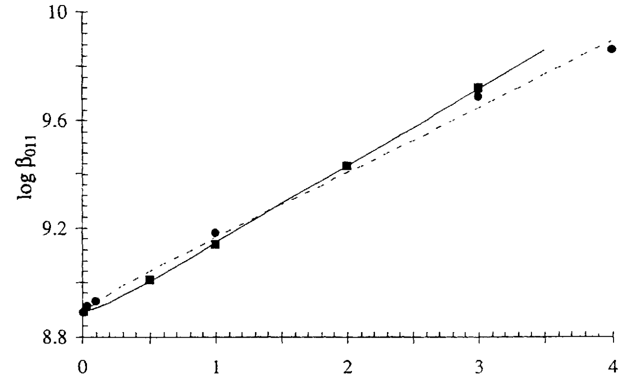

Fig. 5 Variation of $\log \beta_{011}$ with the ionic strength in different media: (– – –) and (●), theoretical function and experimental values in KCl; (—) and (■), theoretical function and experimental values in NaClO$_4$

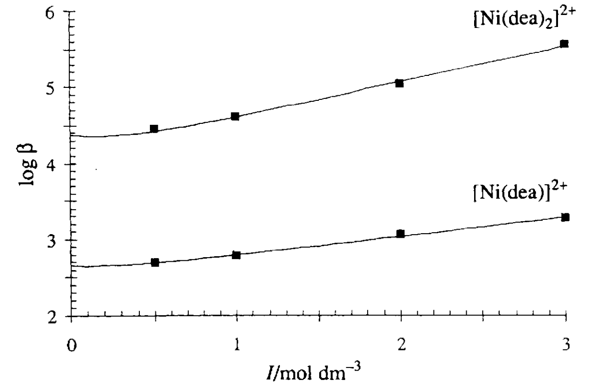

Fig. 6 Variation of $\log \beta_{110}$ and $\log \beta_{120}$ with the ionic strength in NaClO$_4$ medium: (—) theoretical function and (■) experimental values

To appreciate the importance of the chemical model and the nickel(II)–diethanolamine species two molar fraction diagrams have been constructed for two different ionic strengths [Figs. 7(*a*) and 7(*b*)], employing the stability constant values proposed in this work together with that proposed by Baes and Mesmer[18] for nickel(II) hydrolysis. In each figure two systems have been plotted, one where there is only Ni$^{\mathrm{II}}$ and the other one where both nickel(II) and diethanolamine are present. At both ionic strengths, although the presence of diethanolamine does not prevent nickel hydroxide precipitation it takes place at high pH values, so at typical pH values for nickel hydroxide precipitation a large amount of Ni^{2+} is still in solution. From a comparison of both plots two conclusions could be made. On the one hand, as the ionic strength is increased the pH range where nickel hydroxide precipitation does not take place because of the formation of soluble complexes is wider, and on the other hand the species distribution is different from one

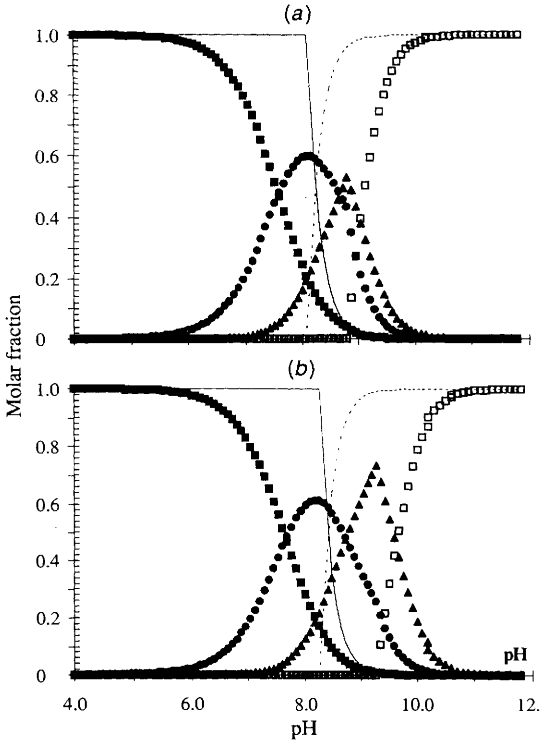

Fig. 7 Molar fraction of nickel(II) species *versus* pH at (*a*) 1.0 and (*b*) 3.0 mol dm^{-3} $NaClO_4$ ionic strength. Lines denote a system with only c_{Ni} = 3.41 × 10^{-3} mol dm^3: (—) Ni^{2+} and (– – –) $Ni(OH)_2$ (solid). Points denote a system with c_{Ni} = 3.41 × 10^{-3} mol dm^3 and c_{dea} = 6.28 × 10^{-2} mol dm^{-3}: (■) Ni^{2+}, (●) $[Ni(dea)]^{2+}$, (▲) $[Ni(dea)_2]^{2+}$ and (□) $Ni(OH)_2$ (solid)

ionic strength to another. These facts could play an important part when chosing a suitable treatment of wastes.

These results, together with those previously obtained[33] and current studies will lead to a thermodynamic model for Ni^{II} in the electroplating system which will hopefully help in the interpretation of the experimental data taken from real samples and in the development of accurate algorithms for the process control and recycling processes.

Acknowledgements

This research was supported by the Government of the Basque Country (project P. G. V. 9230); R. Castaño thanks the Basque Government for a grant.

References

1 R. W. Peters and Y. Ku, *AIChE Symp. Ser.*, 1981, **243**, 9.
2 P. Sanciolo, I. H. Harding and D. E. Mainwaring, *Sep. Sci. Technol.*, 1992, **27**, 375.
3 M. L. Apel, J. Bridges, M. F. Szabo and S. H. Ambekar, *Metals Speciation, Separation and Recovery*, eds. J. W. Patterson and R. Passino, Lewis Publ., Michigan, 1990, vol. 2, p. 516.
4 W. Ying, R. R. Bonk and M. E. Tucker, *J. Hazard. Mater.*, 1988, **18**, 68.
5 R. L. Basset and D. C. Melchior, *ACS Symp. Ser.*, 1990, 416.
6 J. Buffle, *Complexation Reactions in Aquatic Systems: An Analytical Approach*, Ellis Horwood, Chichester, 1988.
7 W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 2nd edn., Wiley, New York, 1981.
8 J. M. Madariaga, *Advances in Recycling Technologies*, eds. H. Hendstrom and H. Skrog, Hutchis, Kopenage, 1993, vol. 2.
9 L. A. Bromley, *AIChE J.*, 1973, **19**, 313.
10 J. M. Madariaga, unpublished work.
11 G. H. Jeffery, J. Basset, J. Mendham and R. C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, 5th edn., Longman, London, 1989.
12 R. Cazallas, L. A. Fernández, N. Etxebarria and J. M. Madariaga, *Lab. Rob. Autom.*, 1993, **5**, 161.
13 F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants*, McGraw-Hill, New York, 1961.
14 G. Gran, *Analyst* (*London*), 1952, **77**, 661.
15 J. L. Fonseca, Licentiate Thesis, University of the Basque Country, 1989.
16 N. Ingri and L. G. Sillén, *Acta Chem. Scand.*, 1962, **16**, 173.
17 C. De Stefano, P. Mineo, C. Rigano and S. Sammartano, *Ann. Chim.* (*Rome*), 1993, **83**, 243.
18 C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, 1976.
19 H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbuhler, *Talanta*, 1985, **32**, 257.
20 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn., Limusa, Mexico, 1986.
21 L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes*, Special Publ. no. 17, The Chemical Society, London, 1964.
22 L. G Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes*, Suppl. I, Special Publ. no. 25, The Chemical Society, London, 1971.
23 D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solutions*, International Union of Pure and Applied Chemistry, London, 1965.
24 D. D. Perrin, *Stability Constants of Metal Ion Complexes*, Part B, Organic Ligands, IUPAC Chemical Data Series No. 22, Pergamon, Oxford, 1979.
25 V. E. Bower, R. A. Robinson and R. G. Bates, *J. Res. Natl. Bur. Stand., Sect. A*, 1962, **66**, 71.
26 J. L. Oscarson, G. Wu, P. W. Faux, R. M. Izatt and J. J. Christensen, *Thermochim. Acta*, 1989, **154**, 119.
27 E. V. Skelenskaya and M. Kh. Karapet'yants, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1966, **11**, 1478.
28 J. Bjerrum and P. Djurdjevic, *J. Indian. Chem. Soc.*, 1982, **59**, 1229.
29 G. A. Bhat and R. S. Subrahmanya, *Indian J. Chem.*, 1973, **11**, 584.
30 N. Etxebarria, L. A. Fernández and J. M. Madariaga, *J. Chem. Soc., Dalton Trans.*, 1994, 3055.
31 G. Arana, N. Etxebarria, L. A. Fernández and J. M. Madariaga, *J. Solution Chem.*, 1995, **24**, 661.
32 N. Etxebarria, J. M. Castresana, M. J. Zapatero, M. A. Olazabal, L. A. Fernández and J. M. Madariaga, *J. Solution Chem.*, 1990, **20**, 1213.
33 R. Castaño, N. Etxebarria and J. M. Madariaga, *J. Chem. Soc., Dalton Trans.*, 1994, 2729.
34 F. A. Long and W. F. McDevit, *Chem Rev.*, 1952, **51**, 119.
35 EXCEL 4.0, Microsoft Corporation, Redmond, WA, 1992.

Received 1*st May* 1995; *Paper* 5/02762D