Asian Journal of Chemistry Vol. 19, No. 1, (2007), 607–615

Potentiometric and Spectroscopic Studies on Nickel(II) 1,4,7,10-tetraazacyclododecane Complexation and Thermodynamic Aspects

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The complex formation equilibria of nickel(II) with 1,4,7,10-tetraazacyclododecane (cyclam, L) were investigated in 0.1 mol L^{-1} ionic strength medium, by KCl at three different temperatures (25°, 35° and 45°C). In this research, potentiometric and spectroscopic titrations were applied that were not performed before in cited studies. The protonation constants of H_2L^{2+} and HL^+ type ions of cyclen were defined; they were in good agreement with other works. The formation constant of NiH_2L^{4+} type complex was determined and thus its occurrence in lower pH range was proved that had not taken place in other Ni(II)-cyclam studies. In higher pH range the existence of NiL^{2+} type complex was identified and its formation constant was defined. It was noticed that the stabilities of either NiH_2L^{4+} and NiL^{2+} complexes decrease with temperature. By means of speciation diagram the existences of NiH_2L^{4+} and NiL^{2+} complexes were also verified. The overall changes in thermodynamic parameters (ΔH, ΔS and ΔG) associated with NiL^{2+} complex formation equilibrium were evaluated graphically.

Key Words: Formation constant, Nickel(II) ion, Potentiometric and spectroscopic methods, Thermodynamic parameters.

INTRODUCTION

There is an increasing interest in metal complexes containing tetraaza macrocycles which have selectivity for the metal ions[1–16]. Cyclam is the smallest member of the tetraaza macrocyclic ligands and forms stable complexes with various metal ions[1–15]. Ni(II) has ionic radii 0.69, 0.63 and 0.83 Å for coordination numbers 4, 5 and 6 respectively[17]. Ni(II) as a d^8 ion can form high spin (octahedral) and low spin (square-planar) complexes with cyclam. The equilibrium between high spin (blue) and low spin (yellow) states was investigated by several authors[6, 7, 10, 16]. Fabrizzi[6] determined that Ni(II) complexes of tetraaza macrocyclic ligands in varying sizes exist in aqueous solution as an equilibrium mixture of a blue high-spin and a yellow low-spin species. They determined the thermodynamic parameters for the blue-to-yellow interconversion of $[Ni(macrocycle)]^{2+}$ complexes; but the formation constants of the complexes formed between Ni(II) ion and cyclen were not determined. Hancock *et al.*[7] applied

UV-Vis spectroscopic technique for the Ni(II) complexes of cyclen and other tetraaza macrocycles. They used an "out-of-cell" potentiometric titration to determine the formation constant for some tetraaza macrocycles including cyclam at 25°C. On the other hand, the stability constant of cyclam complex of Ni(II) was determined spectrophotometrically at 25°C in 2.0 M $NaClO_4$ ionic medium by Kalinka *et al.*[15]

In our study, the potentiometric and spectroscopic titration techniques were used at three different temperatures. Our study originated from interest in the reaction of Ni(II) with cyclam; for our purpose the potentiometric titration, but not out-of-cell potentiometric titration, and spectroscopic titration comparison of two protonation constants of cyclam and the formation constant of Ni(II)-cyclam complex would be possible with the result of Hancock; those were found by spectroscopic technique[7, 10].

EXPERIMENTAL

All the chemicals used were of analytical reagent grade. Sodium hydroxide solution, free from carbonate, was prepared and standardized with potassium hydrogen phthalate. Cyclam (1,4,7,10-tetraazacyclododecane) was purchased from Sigma. The cyclam was synthesized as the hydrocloride salt that has four moles of protons per cyclam molecule and recrystallized according to the method of Atkins *et al.*[18] The content of protonated cyclam (H_4L^{4+}) was periodically checked by Gran titration[19]. The stock solution of Ni(II) ion was prepared by dissolving the proper amounts of nickel(II) chloride hexahydrate (Carlo-Erba, 99%) in a small excess of HCl. Then it was complexometrically standardized[20]. The concentration of free acid in the Ni(II) solution was systematically checked by potentiometric titration before each series of experiments. All solutions were prepared in carbon dioxide free double distilled water.

Potentiometric measurements: The potentiometric titrations were carried out at 25 ± 0.01°C using a Schott pH-meter (Hofheim, Germany); with combined glass electrode the accuracy of pH-meter was ± 0.002 pH unit. It was calibrated to determine the hydrogen ion concentration by known procedures[21, 22]. The ionic strength of the solution was adjusted to 0.1 mol L^{-1} by potassium chloride. The titrations of cyclam alone and Ni(II)-cyclam system were investigated throughout in pH = 2.3–11.0 with standard NaOH. All titrations were performed under saturated nitrogen atmosphere and at least 20 min time intervals were necessary between additions of successive aliquots of sodium hydroxide to reach constancy of pH and they were carried out in triplicate.

Spectrophotometric measurements: The visible spectra of the set of solutions were taken using Shimadzu UV-2100 spectrophotometer (Kyoto, Japan) to define the absorbances of protonated cyclam, Ni(II) ion and Ni(II)-cyclam complex at specific pH value, as a function of wavelength. The solutions of Ni(II)-cyclam system in 1 : 1 mole ratio were prepared in 0.1 mol L^{-1} potassium chloride medium and titrated with NaOH solution. These titrations were performed in thermostated titration cell that was attached to flow-cell of UNICAM UV-2 spectrophotometer (Cambridge, United Kingdom). Then in order to read pH and absorbance values, the solution was allowed to equilibrate for approximately 20 min after addition of NaOH solution in the nitrogen atmosphere.

Calculations: The protonation constants of cyclam (log K), the stochiometries and the formation constants of Ni(II)-cyclam complexes (log β) were calculated by mathematical analysis of the potentiometric titration curves of cyclen and its Ni(II) complex (Tables 1 and 2). The calculated constants were averages of at least thirty calculated values in the defined regions, computer programme RANA that was written by our research group and was described previously[19]. This programme used the criterion for which species are present in equilibria is simply a model of best complex that accounts for each H^+-cyclam and Ni(II)-cyclam. Non-linear least-squares analysis of the data in terms of assumed reactions gave a satisfactory fit in the buffer regions of Ni(II)-cyclam system in 1 : 1 mole ratio. In order to draw the speciation diagrams, the concentrations of the species NiH_2L^{4+} and NiL^{2+} were calculated also by means of RANA computer programme.

RESULTS AND DISCUSSION

Potentiometric studies: Potentiometric titration of protonated cyclen (H_4L^{4+}) was performed in 0.1 mol L^{-1} KCl ionic medium at 25°, 35° and 45°C (Fig. 1, curves I, II and III respectively). The potentiometric titration curve showed only one inflection at a = 2 (a: mmol base per mmol ligand). The second and third protonation constants of cyclam (log K_{HL} and log K_{H_2L}) could be determined with potentiometric titration of H_4L^{4+} (row 2 and row 3 respectively in Table-1). They were in good agreement with the results of other works[9, 23]. Unfortunately the measurements of the protonation constants of L and H_3L^{3+} require considerable efforts, because of the poorer electrode responses. Therefore,

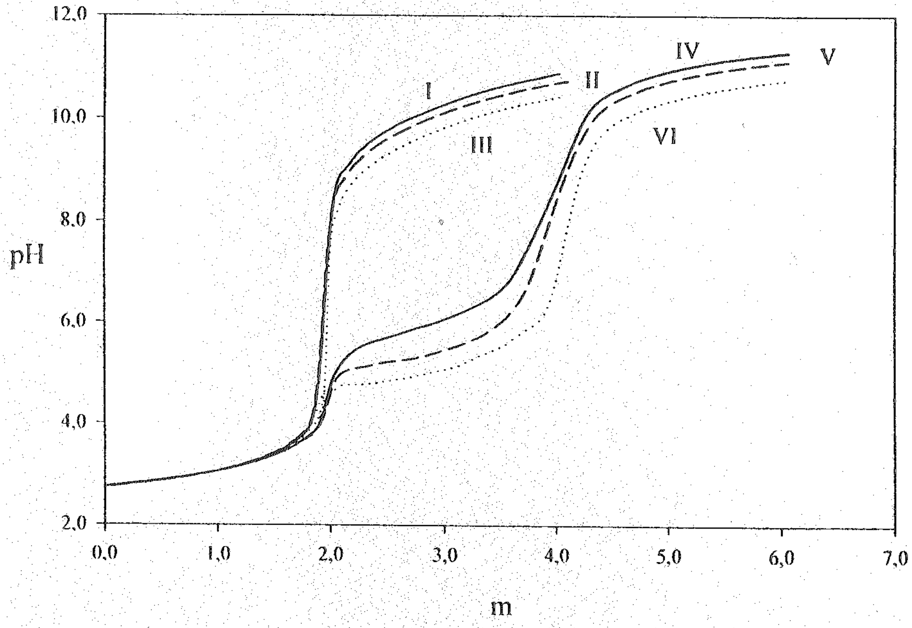

Fig. 1. Potentiometric titration curves of Ni(II) complexes of cyclen in 0.1 mol L^{-1} at 25°C, 35°C and 45°C (**I, II, III**); cyclen alone at **IV, V, VI**; (1 : 1) molar ratio of Ni(II) to cyclam

the reported values of log K_L and log K_{H_3L} were introduced in required equations (row 1 and row 4, respectively in Table-1), while our protonation constants and the corresponding literature values for HL^+ and H_2L^{2+} are in good agreement at 25°C.

TABLE-1
PROTONATION CONSTANTS (log K) OF CYCLAM AT DIFFERENT TEMPERATURES ($I = 0.1$ mol L^{-1})

S.No.	Equilibrium Proton complexes	Cyclam (12ane N_4) log K		
		25°C	35°C	45°C
1.	$L + H^+ \rightleftharpoons HL^+$	11.32[23] 11.27[9]	(11.11)	(10.91)
2.	$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	9.92 ± 0.05* 9.72 ± 0.08[23] 9.96[9]	9.69 ± 0.02*	9.41 ± 0.09*
3.	$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$	2.47 ± 0.20* < 2.3[23] 2.18[9]	2.35 ± 0.15*	2.33 ± 0.27*
4.	$H_3L^{3+} + H^+ \rightleftharpoons H_4L^{4+}$	< 2.3[23] 1.74[9]	~ (< 2.3)	~ (< 2.3)

*This work

Potentiometric titrations of Ni(II) ion and protonated cyclam in (1 : 1) mole ratio were performed in 0.1 mol L^{-1} KCl ionic medium at 25°, 35° and 45°C (Fig. 1, curves IV, V and VI respectively). In the potentiometric titration curves, two different inflections were observed at $m = 2.0$ and $m = 4.0$ (m: mmol base per mmol metal ion) and at each titration point at least 20 min were waited for equilibration after addition of each increment of base. The occurence of equilibrium I (row 1 in Table-2) was assumed since the release of two protons in $m = 0.0$–2.0 range were observed and as a result NiH_2L^{4+} type complex can form. Due to the titration of two more protons in $m = 2.0$–4.0 range, the formation of NiL^{2+} type complex from NiH_2L^{4+} type complex was considered in terms of equilibrium 2 (row 2 in Table-2). In order to calculate log K_1 value in $m = 0.0$–2.0 buffer region (pH = 2.7–3.5 range) and log K_2 value in $m = 2.0$–4.0 buffer region (pH = 4.4–6.5 range), the results of potentiometric titrations were introduced into the derived equations (Table-2, row 1 and row 2). Standard errors found for calculated K_1 and K_2 values are rather low, so they indicate that our assumptions are valid. The existence of NiH_2L^{4+} type complex was noticed in lower pH range (2.7–3.5) and its formation constant (log β') was measured as 5.27 ± 0.04 in 25°C and it drops to 4.92 ± 0.06 in 35°C and 4.01 ± 0.03 in 45°C. In higher pH range (4.4–6.5), the occurrence of NiL^{2+} complex was evaluated to define its formation constant. Then, the mean values of formation constants of Ni(II)-

cyclam complexes (log β) were determined by introducing K_1, K_2 and protonation constants of cyclam for three different temperatures (Table-2, row 4) into the related equations. The existences of the species that occurred as a function of pH values, (Ni^{2+}, NiH_2L^{4+} and NiL^{2+}) were also verified by speciation diagram for three different temperatures; but for simplicity only one speciation diagram at 25°C is given (Fig. 2).

TABLE-2
LOGARITHMS OF EQUILIBRIUM CONSTANTS (log K) AND FORMATION CONSTANTS (log β) OF Ni(II) COMPLEXES WITH CYCLAM AT DIFFERENT TEMPERATURES BY POTENTIOMETRIC AND SPECTROSCOPIC METHOD ($I = 0.1$ mol L^{-1})

S.No.	Ni(II)-cyclam complexes			
	Equilibrium	Temp. (°C)	Potentiometric method	Spectroscopic method
			$\log K_1$	
1.	$Ni^{2+} + H_4L^{4+} \rightleftharpoons NiH_2L^{4+} + 2H^+$	25	0.50 ± 0.04	–
		35	0.27 ± 0.06	–
		45	-0.62 ± 0.03	–
			$\log K_2$	
2.	$NiH_2L^{4+} \rightleftharpoons NiL^{2+} + 2H^+$	25	-11.49 ± 0.06	-11.12 ± 0.07
		35	-10.96 ± 0.04	-10.52 ± 0.08
		45	-10.01 ± 0.05	-9.16 ± 0.03
			$\log \beta'$	
3.	$Ni^{2+} + H_2L^{2+} \rightleftharpoons NiH_2L^{4+}$	25	5.27 ± 0.04	–
		35	4.92 ± 0.06	–
		45	4.01 ± 0.03	–
			$\log \beta$	
4.	$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	25	15.03 ± 0.05	15.40 ± 0.06
		35	14.76 ± 0.05	15.20 ± 0.07
		45	14.32 ± 0.04	15.17 ± 0.03

The mean values of formation constant (log β) for NiL^{2+} complex were found by potentiometric titrations for three different temperatures, respectively. While the stability of linear polyamine complex of Ni(II)-2,2,2-tet is 13.8 at 25°C in 0.1 mol L^{-1} ionic medium[24], that value is 1.23 unit lower than the formation constant of Ni(II)-cyclam complex by calculated potentiometric method which reflects the high thermodynamic stability of Ni(II)-cyclam complex.

Spectroscopic studies: The electronic spectra of cyclam, Ni(II) and Ni(II)-cyclen solutions were taken in 400–800 nm range (Fig. 3). The most appropriate working wavelength for Ni(II)-cyclam complex was found as 562 nm. Then absorbances of Ni(II)-cyclam solutions were measured at 562 nm in the pH range 4.4–6.5 by spectroscopic titration in which the NiL^{2+} complex formed at an ionic strength of 0.1 mol L^{-1} potassium chloride and the absorbance measurements

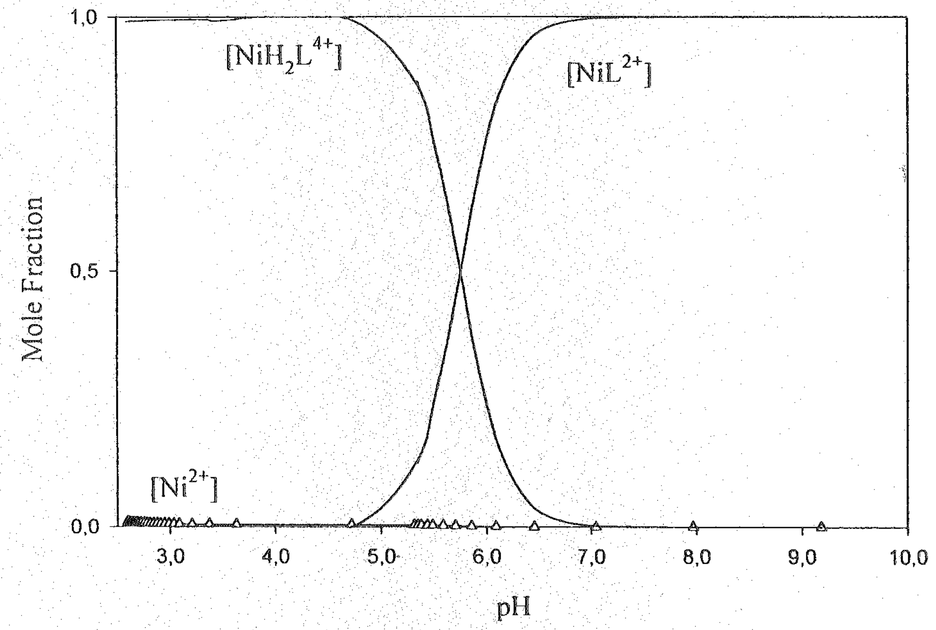

Fig. 2. Species distribution curves of the Ni(II) ion and Ni(II)-cyclam system as a function of $-\log [H^+]$, for a solution initially containing 9.51×10^{-4} mol L^{-1} cyclam and 9.51×10^{-4} mol L^{-1} Ni(II) ion (T = 25°C and I = 0.1 mol L^{-1} KCl)

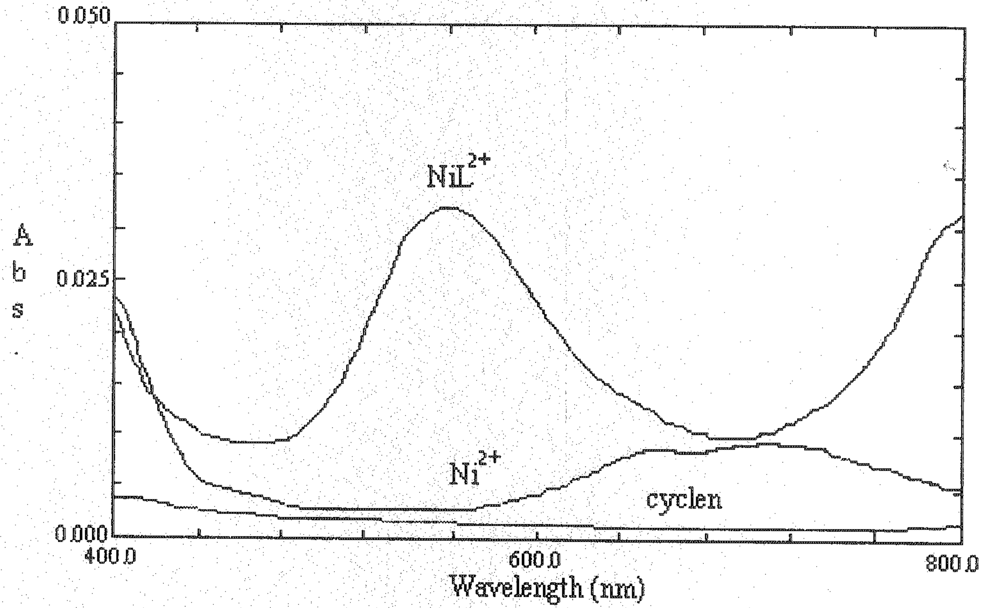

Fig. 3. Absorption spectra of Ni(II), cyclam and Ni(II) complex of cyclam in 0.1 mol L^{-1} KCl at 25°C (pH = 6.10); Ni(II): $T_{Ni} = 3.63 \times 10^{-3}$ M; cyamen: $T_L = 3.63 \times 10^{-3}$ M; Ni(II)-cyclam: $T_{Ni} = T_L = 3.63 \times 10^{-3}$ M

were repeated at three different temperatures. The measured absorbance and pH values that belong only to complex NiL^{2+} formed by equilibrium 2 (row 2 in Table-2) were introduced into the found equation by means of Agreen's approach[25]. According to Agreen's approach ε_{NiL} and β values can be determined from the plot of $T_{Ni^{2+}}/A$ values against the $[H^+]^2$ ratio (Fig. 4). The spectroscopically determined formation constants of NiL^{2+} complex for three different temperatures were tabulated in Table-2. Hancock *et al.*[7] determined the formation constant for NiL^{2+} complex as 14.0 for low spin and 16.4 for high spin complex

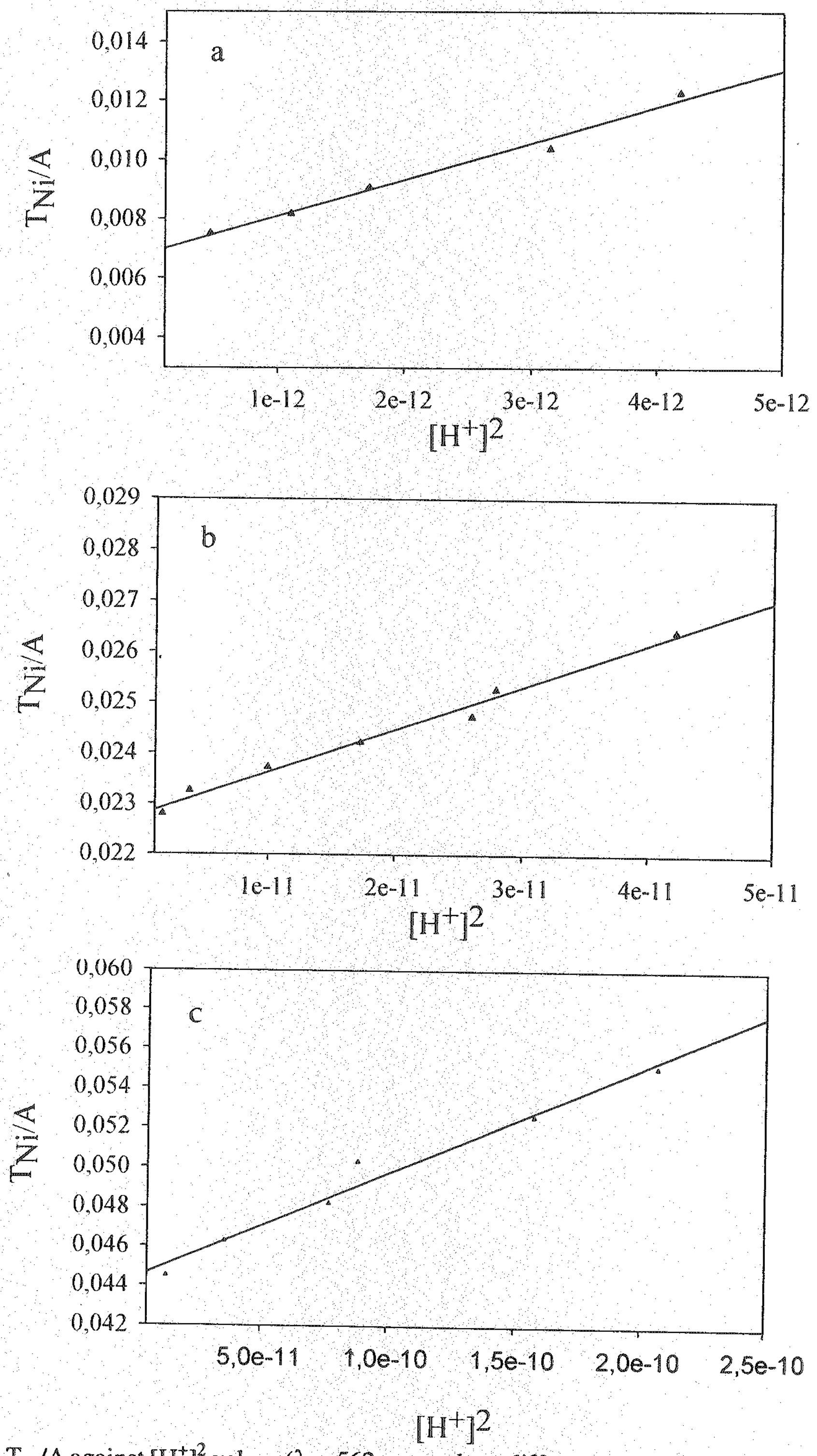

Fig. 4. T_{Ni}/A against $[H^+]^2$ values ($\lambda = 562$ nm, at three different temperatures: a: 25°C; b: 35°C; c: 45°C).

in 0.1 mol L^{-1} ionic medium. Kalinka *et al.*[15] calculated the formation constant for NiL^{2+} complex as 16.4 in 2.0 M $NaClO_4$ ionic medium.

While the mean values of log β calculated spectroscopically are 15.40 ± 0.06, 15.20 ± 0.07 and 15.17 ± 0.03, for 25°, 35° and 45°C respectively, our formation constant (log $\beta = 15.03 \pm 0.05$) determined potentiometrically at 25°C is roughly equal to Hancock's average value (log β = 15.20) that was defined by out-of-cell method which waited for four weeks.

Thermodynamic parameters: The values of overall changes in free-energy (ΔG), in enthalpy (ΔH) and in entropy (ΔS) for Ni(II)-cyclam formation equilibria were determined by the help of Gibbs-Helmholtz equation[26] for potentiometric results. The formation constant of NiL^{2+} complex (row 4 in Table-2) was calculated at three different temperatures and plot of log β against 1/T resulted in a straight line indicating that ΔH is constant at different temperatures (Fig. 5). ΔH was determined by equating slope of the graph to –ΔH/R. Fabbrizzi *et al.*[16] reported that the formation entalphy of Ni(II)-cyclam complex involved more than 99% of the high spin form. Our graphically found ΔH value is higher than the cited value by Fabbrizzi *et al.*[16] and Hancock *et al.*[7] (Table-3).

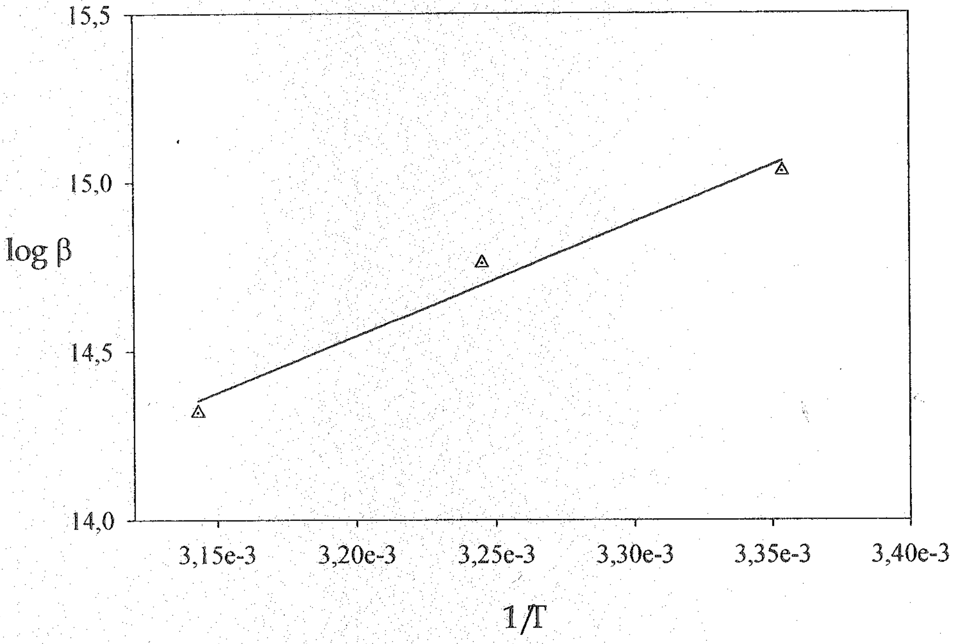

Fig. 5. log β values at different temperatures against 1/T values

TABLE-3
THERMODYNAMIC PARAMETERS OF COMPLEX OF NI(II) WITH CYCLAM (IN 0.1 mol L^{-1} KCl)

Temp. (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K mol)
25	–85.77* –93.68[7] (a) –82.09[7] (b)	–64.22* –49.79[16] (a) –47.82[7] (a)	72.26* 154.14[7] (a)
35	–87.07*		74.14*
45	–87.19*		72.22*

* This work. In Ref. 7: 0.5 mol L^{-1}. (a) high spin. (b) low spin.

This discrepancy is probably arising from the differences in experimental conditions since they determined ΔH values calorimetrically not potentiometrically. The overall changes in entropy of reaction (ΔS) were defined at three different temperatures. The values of overall changes in free-energy (ΔG), entalpy (ΔH) and entropy (ΔS) were tabulated in Table-3. The thermodynamic parameters (ΔH, ΔS and ΔG) associated with formation equilibria of NiL^{2+} complex defined the values of Hancock[7]. These thermodynamic parameters (ΔG and ΔH) are in accordance with the changes of investigated equilibrium.

ACKNOWLEDGEMENTS

The instruments of this research were supplied by the Alexander Von Humboldt Foundation, to whom the authors wish to express their thanks.

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(*Received*: 29 December 2005; *Accepted*: 30 June 2006) AJC-4985