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Potentiometric and Spectrophotometric Investigations of Nickel-Triethanolamine Complexes

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A detailed study of nickel-triethanolamine complexes has been made employing potentiometric and spectrophotometric methods. The potentiometric method has been used to investigate the conditions for the formation of both mono- and polynuclear complexes. The formulae and the stability constants of the following complexes have been determined $Ni(TEA)^{2+}$, $Ni(TEA)_2^{2+}$, *and* $Ni_2(TEA)_2^{4+}$. *Absorption spectra of pure mononuclear complexes have been computed by the combination of potentiometric and spectrophotometric methods. The results are discussed on the basis of ligand field theory. Comparison of the step constants of the nickel-ethanolamines (mono-, di- and tri-) shows a slight chelate effect in these complexes due to coordination through hydroxyl oxygen. In the case of polynuclear complexes it is likely that bridging occurs through hydroxyl oxygen.*

Introduction

Sklenskaya and Karapetyants[1] have given the stepwise formation constants of nickel-triethanolamine complexes of formulae $Ni(TEA)^{2+}$, $Ni(TEA)_2^{2+}$, $Ni(TEA)_3^{2+}$. Woodburn and Magee[2] haeve measured the absorption spectra of a nickel-triethanolamine system containing a metal to ligand ratio 1:200 and have identified the following transitions.

$$^3A_{2g}\rightarrow{}^3T_{1g}(P);\ ^3A_{2g}\rightarrow{}^3T_{1g}(F)$$

They have also mentioned that a charge-transfer band occurs below 200 mμ. However, there has been no detailed investigation of the nature of the absorption spectra of individual complexes nor conditions for the formation of polynuclear complexes. In the present paper a detailed potentiometric and spectrophotometric investigation of the nickel-triethanolamine system has been undertaken with a view to elucidating the nature of mono- and polynuclear complexes formed and the interpretation of the absorption spectra of mononuclear complexes on the basis of ligand field theory.

Experimental Section

1) *Potentiometric Method.* The experimental conditions of the work are summarized in Table I.

For titrations under Bjerrum conditions[3] experiments were done employing 0.1 *M*, 0.3 *M*, 0.5 *M*, and 1.0 *M* triethanolammonium ion and various concentrations of nickel ion (15 to 30 m*M*). Titration was carried out by adding triethanolamine to a mixture of triethanolammonium ion and nickel ion (nitrate). During the course of the titration the concentration of nickel ion and triethanolammonium ion was maintained constant by the suitable addition of nickel and triethanolammonium ion as described by Sillen[4] in hydrolytic studies. The total ionic strength was maintained at 1 *M* by adding sodium perchlorate, in 0.1 *M*, 0.3 *M*, and 0.5 *M* TEA ion solutions (TEA - triethanolamine).

For studying the polynuclear complex formation, in the higher concentration range of the metal ClO_4^- concentration was maintained constant at 3 *M* as used by Sillen[4] in hydrolytic studies. As already mentioned the concentration of metal ion and TEA ion was maintained constant by the suitable addition of nickel and triethanolammonium ion.

All pH measurements were made employing Radiometer pH-meter (PHM 4C) with external glass electrode. The temperature was maintained 30°±.1°C during the titration.

2) *Spectroscopic Method.* Absorption spectra were taken employing Hilger UVSPEK in ultra violet and visible regions, the temperature being 30±2°C. A UNICAM spectrophotometer type SP 700 A, was used to measure the spectra between 800 mμ and 1250 mμ.

Calculations

The following equations are employed for calculating $\bar{n}$ and pA values in Bjerrum titrations.

pA = $-\log A_t$+drop in pH due to complex formation

$$\bar{n}=\frac{A_t-[A]}{C_M}$$

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(1) E.V. Sklenskaya and M.Kh. Karapetayants, *Russ. J. Inorg. Chem.*, 1478 (1967).

(2) S.I. Woodburn and R.J. Magee, *Aust. J. Chem.*, *20*, 439 (1967).

(3) J. Bjerrum, « Metal aminc formation in aqueous solution », Publ. P. Hasse and Son, 1957.

(4) K.A. Burkov, L.S. Lilic, and L.G. Sillen, *Acta Chem. Scand.*, *19*, 14 (1965).

Table I.

Nature of the complex	Experimental conditions conc. of metal ion.	conc. of triethanolammonium ion.	ionic strength
Mononuclear complex	(a) 15 mM to 30 mM	0.1M, 0.3M, 0.5M and 1.0M.	1 M by the addition of perchlorate
Polynuclear Complex	(b) 10 mM to 40 mM	5 mM	1 M by the addition of perchlorate.
	(c) 50 mM to 300 mM	10 mM	ClO_4^- concentration maintained constant at 3 M

Where A_t - total concentration of triethanolamine. C_M - total concentration of the metal ion.

In the case of polynuclear complexes, the free ligand concentration is determined employing the equation[3]

$$[A]=10^{-pK}\frac{[HA^+]}{[H^+]}$$

The pH range in these experiments is quite small (6.3 to 7) and the concentration of HA^+ is regarded as practically constant even though its concentration is quite low (5 mM and 10 mM). After determining the value of [A], the value of $\bar{n}$ is calculated using the expression given above. The total ionic strength was maintained at 1 M with perchlorate when the concentration range of the metal was 10 to 40 mM and the concentration of perchlorate ion was maintained at 3 M in experiments in which the concentration of the metal ion was 50 to 300 mM. The pK value under the conditions of the experiment was 7.89±0.01 in 0.005 M TEA–ClO_4 in solutions of 1 M ionic strength and 8.25±0.02 in 0.01 M TEA–ClO_4 in 3 M ClO_4^-.

Results

(1) *Potentiometric Studies of Nickel-triethanolamine Complexes.* (i) $\bar{n}$–pA curves using Bjerrum's Technique. The $\bar{n}$–p(TEA) or $\bar{n}$–(pA) curves obtained at various metal ion concentrations employing 0.1 M, 0.5 M, and 1.0 M triethanolammonium ion are given in Figure 1. Curves obtained with 0.3 M triethanolammonium ion are similar to those obtained in 0.1 and 0.5 M solutions. In the curves presented the values of $\bar{n}$ at different pA values, for various metal ion concentrations are given. All the points marked as "●" refer to one metal ion concentration (15 mM).

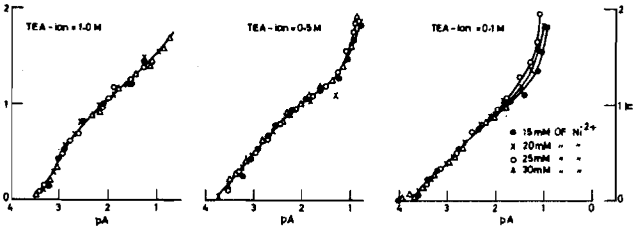

Figure 1. $\bar{n}$-pA curves of nickel-triethanolamine system at various concentrations of triethanolammonium ion under Bjerrum conditions. In 0.5 M and 0.1 M triethanolammonium ion solutions the branching of $\bar{n}$-pA curves occurs at $\bar{n}$, 1.5 and 1.0 respectively.

Similarly x, o and Δ points refer to 20 mM, 25 mM and 30 mM respectively. Each set of points corresponding to a single metal ion concentration forms a curve. The curves obtained at various metal ion concentrations are merging one upon the other within the limits of the experimental error. Hence a single curve is drawn. This coincidence is upto about $\bar{n}$ = 1.5 in 1.0 M and 0.5 M and $\bar{n}$ = 1 in 0.1 M solutions.

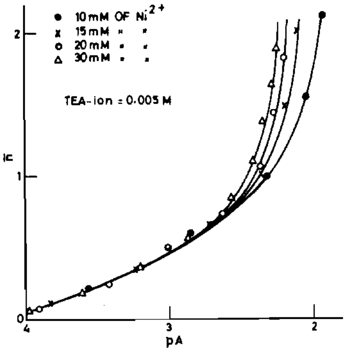

Figure 2. $\bar{n}$-pA curves of nickel-triethanolamine system in the case of polynuclear complex formation (lower metal ion concentration range).

(ii) $\bar{n}$–pA curves of titrations with metal to ligand ratio ⩾2.

(a) Lower metal ion concentration range (Table Ib). Typical n–pA curves are presented in Figure 2. These curves coincide up to $\bar{n}$ = 0.7. Beyon $\bar{n}$ = 0.7, they branch out and rise rapidly. The values of $\bar{n}$ are obtained till precipitation occurs.

(b) Higher metal concentration range (Table Ic). Data obtained under ii (a) (Figure 2) indicate that mononuclear complexes are produced until $\bar{n}$ reaches a value of 0.7 and afterwards polynuclear complexes are produced. In order to produce only polynuclear complexes, experiments have been conducted using higher metal ion concentrations *viz.* 50 mM to 300 mM. The concentration of TEA ion is kept at 10 mM (as at lower concentrations of TEA-ion, precipitation occurs at low $\bar{n}$ values). The $\bar{n}$–pA curves obtained are presented in Figure 3.

(2) *Absorption Spectra of Nickel-triethanolamine Complexes.* If a mononuclear system contains two complexes MA and MA_2, the formation function takes the following form

$$\bar{n}+(\bar{n}-1)\beta_{11}[A]+(\bar{n}-2)\beta_{12}[A]^2=0$$

On rearranging one gets,

$$\frac{\bar{n}}{(1-\bar{n})[A]}=\frac{(2-\bar{n})\beta_{12}}{(1-\bar{n})}[A]+\beta_{11}$$

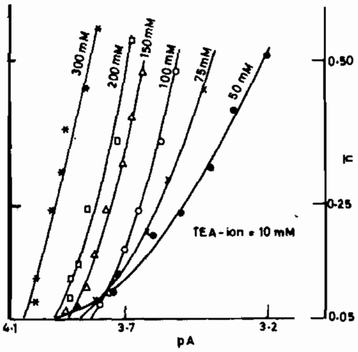

Figure 3. $\bar{n}$–pA curves of nickel-triethanolamine system in the case of polynuclear complex formation (higher metal ion concentration range).

It is, therefore, clear that if the plot of $\frac{\bar{n}}{(1-\bar{n})[A]}$ *vs.* $\frac{(2-\bar{n})}{(1-\bar{n})}[A]$ is a straight line having a positive slope, one can conclude that the system contains two mononuclear complexes. In the present system the plot of $\frac{\bar{n}}{(1-\bar{n})[A]}$ *vs.* $\frac{(2-\bar{n})}{(1-\bar{n})}[A]$ is a straight line with a positive slope (Figure 4). On the basis of the potentiometric data it can therefore be concluded that nickel forms with triethanolamine only two mononuclear complexes, *viz.*, $Ni(TEA)^{2+}$ and $Ni(TEA)_2^{2+}$. The pure spectra of these complexes in the ultraviolet and in the visible regions is obtained by the graphical method employed by Mahapatra and Subrahmanya[5] by combining potentiometric and spectrophotometric data. The method consists of determining the molecular extinctoin coefficients (ε_m) at various values of $\bar{n}$, calculating the fraction of the different species (*i.e.* α_0, α_1, α_2 referring to Ni^{2+}, $Ni(TEA)^{2+}$ and $Ni(TEA)_2^{2+}$ respectively) from the stability constants and plotting suitable linear equations from which individual molecular extinction coefficients could be read.

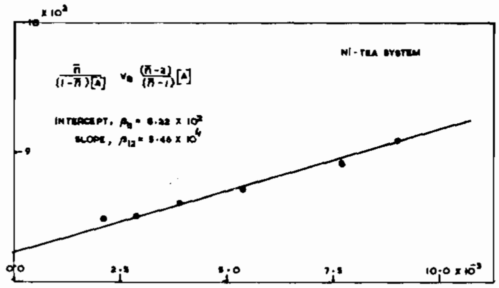

Figure 4. Analysis of the $\bar{n}$-pA curves under Bjerrum conditions.

In the region $0.3<\bar{n}<0.8$, the species that can be expected to be present are Ni^{2+}, $Ni(TEA)^{2+}$ and $Ni(TEA)_2^{2+}$ and when $\bar{n}$ is less than 0.3 only Ni^{2+} and $Ni(TEA)^{2+}$ can be present. The following equations hold for the two regions of $\bar{n}$,

$$\varepsilon_m=\alpha_0\varepsilon_0+\alpha_1\varepsilon_1(\bar{n}<0.3)$$

or

$$\text{or}\quad \frac{\varepsilon_m}{\alpha_1}=\frac{\varepsilon_0\alpha_0}{\alpha_1}+\varepsilon_1 \tag{1}$$

$$\varepsilon_m=\alpha_0\varepsilon_0+\alpha_1\varepsilon_1+\alpha_2\varepsilon_2(0.3<\bar{n}<0.8)$$

or

$$\text{or}\quad \frac{\varepsilon_m-\alpha_0\varepsilon_0}{\alpha_1}=\varepsilon_2\frac{\alpha_2}{\alpha_1}+\varepsilon_1 \tag{2}$$

It is clear that from the plots of (i) $\frac{\varepsilon_m}{\alpha_1}$ *vs.* $\frac{\alpha_0}{\alpha_1}$ and (ii) $(\varepsilon_m-\alpha_0\varepsilon_0)/\alpha_1$ *vs.* α_2/α_1, the values of ε_0, ε_1, and ε_2 can be determined. Typical plots corresponding to equation (2) are given in Figure 5 and the absorption spectra in the ultraviolet and visible regions are given in Figure 6. Detailed analysis in the near infrared region has not been done since the measurements on the recorded spectra could not be carried out accurately. Hence in the inset on Figure 6 it is shown as 'qualitative' and refers to the predominant species.

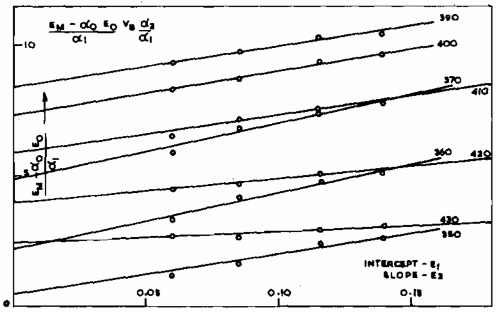

Figure 5. Typical plots corresponding to equation (2).

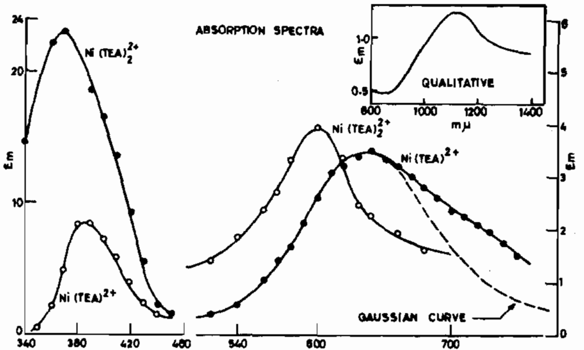

Figure 6. Absorption spectra of individual nickel-thiethanolamine complexes. ('Qualitative' refers to only predominant species).

[5] S. Mahapatra and R.S. Subrahmanya, *Proc. Ind. Acad. Sci.*, *59A*, 299 (1964).

Discussion

1. *Nature of the Complex Formation in Case of Bjerrum's Titration Method.* When a system contains mononuclear complexes both pure and hydroxy (MA_j, $MA_j(OH)_i$) and polynuclear complexes both pure and hydroxy (M_mA_j; $M_mA_j(OH)_i$ the following equation gives the relationship between $\bar{n}$ and pA.[6]

$$\bar{n}=\frac{\sum_{m=1}\sum_{j=1} j\beta_{mj}[M]^{m-1}[A]^j+\sum_{m=1}\sum_{j=1}\sum_{i=1} j\beta_{mji}[M]^{m-1}[A]^j[OH]^i}{1+\sum_{m=1}\sum_{j=1} m\beta_{mj}[M]^{m-1}[A]^j+\sum_{m=1}\sum_{j=1}\sum_{i=1} m\beta_{mji}[M]^{m-1}[A]^j[OH]^i}$$

When both pure and mixed hydroxy mono- and polynuclear complexes are present $\bar{n} = f\{[A],[OH],[M]\}$. It is found that when $\bar{n}<1$, $\bar{n}$–pA curves plotted for various metal concentrations at any particular concentration of TEA and at various concentrations of TEA ion for a single metal ion concentration coincide indicating that only pure mononuclear complexes are formed. The values of β_{11} and β_{12} as obtained from the intercept and the slope of the plot of $\bar{n}/(1-\bar{n})[A]$ *vs.* $(2-\bar{n})/(1-\bar{n})$ $[A]$ (Figure 4) are $10^{2.92}$ and $10^{1.82}$ respectively.

$$\frac{\bar{n}}{(1-\bar{n})[A]}\ Vs.\ \frac{(2-\bar{n})}{(1-\bar{n})}[A]$$

The formation curves for $\bar{n}>1$ in 0.1 *M*, 0.3 *M* and 0.5 *M* TEA ion solutions and $\bar{n}>1.5$ in 1.0 *M* TEA ion solutions do not coincide not only in solutions containing different metal ion concentrations but also in solutions containing different TEA ion concentration at constant concentration of the metal ion. Further, the $\bar{n}$ values increase rapidly in this region. It has been pointed out previously[5] that at constant value of pA, the value of n obtained depends upon the pH of the solution. If mixed hydroxy complexes are produced, a higher value of n is obtained if the pH is higher. Consequently, a steep rise in $\bar{n}$–pA curves can only be interpreted as due to the formation of mixed hydroxy complexes. Also the $\bar{n}$–pA curves at various metal ion concentrations do not coincide. Both these factors put together suggest that polynuclear mixed hydroxy complexes are formed.

2. *Analysis of $\bar{n}$–pA Curves from Titrations with Metal-ligand Ratio $\geqslant 2$.*

(a) Lower metal ion concentration range (Table Ib). Examination of the $\bar{n}$–pA curves presented in Figure 2, indicates the formation of only mononuclear complex till about $\bar{n} = 0.7$. There after the $\bar{n}$–pA curves do not coincide indicating the formation of polynuclear complexes. Since mononuclear complexes are giving place to polynuclear ones, it can be concluded that mono- and polynuclear complexes will be present together in the polynuclear region. The analysis of the polynuclear portion therefore becomes extremely complicated. Hence no attempt has been made to identify the nature of the complexes nor obtain their stability constants.

(b) Higher metal ion concentration range (Table Ic). The results have been analyzed on the basis of the formation of one predominant complex,[4] $M_q\ A_p$. Since the $\bar{n}$ values are low the final expression is simplified by approximating $[M] = C_M$. The expression for the formation function on rearrangement can be written thus:

$$\log(\bar{n}C_{Ni})=p\ \log[A]+\log\ p+\log\beta_{qp}+q\ \log C_{Ni}$$

The slope of the plots of $\log(\bar{n}C_{Ni})$ *vs.* $\log[A]$ gives the value of "p". The values of $(\log\ p+\log\ \beta_{qp}+q\ \log\ C_{Ni})$ for various values of C_{Ni} are computed at a suitable fixed value of $(\bar{n}C_{Ni})$. The values of $\log\ \beta_{qp}$ are calculated for different assumed values of "q". From the constancy of the values of $\log\ \beta_{qp}$, the formula and the stability constant of the complex are obtained.

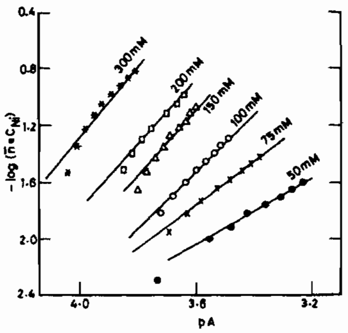

Figure 7. Analysis of ñ-pA curves of polynuclear complexes formed under "self-medium" conditions.

The plot of $\log(\bar{n}C_{Ni})$ *vs.* pA (Figure 7) in the concentration range 50 to 300 m*M* indicates that its slope increases with an increase in the metal ion concentration. From 100 m*M* and above, the slope is 2 indicating that the value of "p" is 2. The values of β for different values of "q" are given in Table II. It is clear that the value of "q" is 2. The formula of the complex in this region is $Ni_2(TEA)_2^{4+}$ and the stability constant is $10^{7.4\pm0.1}$. In solutions containing less than 100 m*M* of the metal ion both mono- and dinuclear complexes are present in different proportions.

Table II. Values of log β for various assumed values of q.

C_{Ni}(Molar)	q=1 $\log\beta_{q2}$	q=2 $\log\beta_{q2}$	q=3 $\log\ \beta_{q3}$
0.100	6.379	7.380	8.380
0.150	6.727	7.450	8.725
0.200	6.692	7.390	8.090
0.300	6.997	7.520	8.040

Average $\log\ \beta_{22} = 7.45\pm0.1$

3. *Absorption Spectra of Pure Mononuclear Nickel-Triethanolamine Complexes.* In the spectra of these complexes three transitions, as expected for a d^8 system have been observed.

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(6) S. Mahapatra and R.S. Subrahmanya, *ibid.*, *58A*, 161 (1963).

	λ_{max}	
	$Ni(TEA)^{2+}$	$Ni(TEA)_2^{2+}$
${}^3A_{2g} \rightarrow {}^3T_{2g}$ (near infrared region):	1100 mμ	—
${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ visible region):	635 mμ	600 mμ
${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ultraviolet region).	387 mμ	370 mμ

These transitions are Laporte forbidden transitions and are due to vibronic coupling. Gaussian analysis for $Ni(TEA)^{2+}$ indicates the presence of two transitions in the middle band. On the curve the second peak has taken the form of a shoulder. The appearance of double peaks in the middle band is indicated by the Gaussian analysis, in $Ni(TEA)^{2+}$ complex appears to be due to the nearness[7] of the ${}^1E_g$ state coming from ${}^1D$ state and ${}^3E_{1g}$ (F) state coming from the ${}^3F$ state resulting in the spin orbit interaction and consequent division of the intensity between the two states giving rise to two peaks.

4. *General Nature of the Nickel Complexes of Mono-, Di- and Triethanolamines.* In order to obtain the nature of bonding in nickel-triethanolamine complex on the basis of successive formation constants it would be necessary to compare the stepwise constants of triethanolamine with those of mono- and diethanolamines, since there is gradation from mono-to-triethanolamine. The nature of bonding in monoethanolamine complex can be obtained by the comparison of the stepwise constants of monoethanolamine with those of ammonia.

The stepwise formation constants (Table III) of the mononuclear ethanolamine (mono-, di- and tri-) complexes obtained[8,9] by this investigation along with those of ammonia complexes given by Bjerrum[3] are given below. Comparison of the nickel-ammonia complexes with those of nickel-monoethanolamine complexes indicates that the stepwise formation constants for $Ni(MEA)^{2+}$, $Ni(MEA)_2^{2+}$, $Ni(MEA)_3^{2+}$ and $Ni(MEA)_4^{2+}$ are greater than the corresponding values of nickel-ammonia complexes while the constant for $Ni(MEA)_5^{2+}$ is smaller than that of $Ni(NH_3)_5^{2+}$.

These values are indicative of the fact that in complexes, $Ni(MEA)^{2+}$ to $Ni(MEA)_4^{2+}$, there is a slight chelate effect. The lower value of the constant for $Ni(MEA)_5)^{2+}$ as compared with $Ni(NH_3)_5^{2+}$, indicates that the monoethanolamine behaves as a monodentate ligand and being a primary amine, the formation constant is lower than that of the corresponding ammonia complex. It may be pointed out that it would have been more appropriate to compare constants of nickel-ethylamine complexes instead of nickel-ammonia complexes with those of nickel-monoethanolamine complexes. Unfortunately the constants of nickel ethylamine complexes are not available. However, one could expect nickel-ethylamine constants to be lower than those of nickel-ammonia complexes. Hence the conclusion arrived at is quite valid.

Table III. Log of stepwise constants for nickel-ammonia, $Ni(MEA)_i^{2+}$, $Ni(DEA)_i^{2+}$ and $Ni(TEA)_i^{2+}$, complexes.

Type of complex	$Ni(NH_3)_i$	$Ni(MEA)_i$	$Ni(DEA)_i$	$Ni(TEA)_i$
NiA	2.73	3.18	2.79	2.915
NiA_2	2.18	2.86	1.63	1.821
NiA_3	1.67	1.72	1.18	—
NiA_4	1.13	1.47	—	—
NiA_5	0.69	0.47	—	—
NiA_6	0.03	0.33	—	—

(MEA - monoethanolamine; DEA - diethanolamine; TEA triethanolamine)

The formation constants of nickel-diethanolamine and triethanolamine complexes are also included in the same table. Since $Ni(DEA)_3^{2+}$ and $Ni(TEA)_2^{2+}$ are the highest complexes produced, it is reasonable to conclude that slight chelate effect will be present in these complexes. However, it is not possible to draw conclusions on the basis of step constants, since the step constants of nickel-diethylamine and triethylamine are not available in literature. It is also likely, particularly in triethanolamine, the steric effects might be responsible for the non-formation of higher complexes.

It is expected that with an increase in the number of ethanol groups in the amine, the successive formation constants of all complexes (1:1, 1:2, 1:3) should decrease. In the present study this is true in the case of the nickel-mono- and diethanolamine complexes. In the case of the nickel-triethanolamine system the constants are slightly higher than those of the Ni–DEA system. This is probably due to the stronger chelate effect in the case of nickel-triethanolamine system.

In the nickel-ethanolamine system quite a few polynuclear complexes have been identified:[6,9]

$$Ni_2(MEA)_2^{4+},\ Ni_3(MEA)_3^{6+},\ Ni_2(DEA)^{4+},\ Ni_3(DEA)_3^{6+},\ \text{and}\ Ni_2(TEA)_2^{4+}.$$

Although there is no direct experimental evidence on the basis of the results presented in this paper, it can be presumed that bridging is perhaps occurring via the ethanolic hydroxyl group as is evident from the fact that the ethanolic hydroxyl group is capable of forming bond through the oxygen of the hydroxyl as indicated by the chelate effect described above.

There is a gradation in the tendency to form polynuclear complexes even under Bjerrum conditions as one proceeds from mono- to di- and to triethanolamine at pH values close to their pK values. It was found that nickel-monoethanolamine system[5] does not produce any polynuclear complexes, whereas polynuclear complexes are produced in the case of diethanolamine at $\bar{n} = 2.2$. In the case of triethanolamine, however, polynuclear complexes are produced at $\bar{n} = 1.0$.

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(7) C.K. Jorgensen, *Acta Chem. Scand.*, *9*, 1362 (1955).

(8) G.A. Bhat and R.S. Subrahmanya, *J. inorg. nucl. Chem.*, 33, 3487 (1971).

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