3072 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3072—3076 (1973) [Vol. 46, No. 10

Polarographic Study of the Substitution Reactions between Nickel(II) Ions and Copper(II) Chelates of Triethylenetetraminehexaacetic Acid

Md. Shamsul HAQUE and Miloslav KOPANICA*
Department of Chemistry, Bangladesh Agricultural University, Mymensingh, Bangladesh
**J. Heyrovsky Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia*

(Received September, 30, 1972)

The mechanism of substitution reaction between nickel ion and Cu–TTHA chelate was studied by polarographic technique. During the study of the substitution reaction the existence of mixed binuclear chelate CuXNi^{2-} was verified and the value of the stability constant was calculated on the basis of polarographic data. Formation of the mixed binuclear chelate was further verified by the amperometric titration of the equimolar mixture of both metal ions with TTHA. Finally the existence of mixed binuclear chelate CuXNi^{2-} was verified by potentiometric titration method. When nickel is present in large excess the replacement of Cu^{2+} ions from Cu$_2$X^{2-} occurred directly without formation of intermediate mixed binuclear chelate. The stability constant of Cu$_2$X^{2-} was calculated from equilibrium study.

The practical utility of EDTA as a titrant for metal ions and in some other fields has encouraged the researchers for ligands with a greater affinity and selectivity for metal ions. One fruitful approach has been the study of higher homologs of EDTA, such as DTPA and TTHA. Their acid dissociation constants were determined by Frost[1] while Grimes *et al.*[2] reported the formation constants of alkaline earth metal chelates with TTHA. The analytical application of TTHA has been studied by Pribil and Vesely[3] mainly in complexometric titration. The interaction between TTHA and various metal ions in aqueous solution was studied by many authors who used mostly potentiometric method[4–8] and in some cases they employed polarographic measurement[9–11] and the stability constants of the metal chelates of TTHA are reported.

During last decade a great interest has been given to study the nature and the mechanism of the electrophilic substitution reaction involving metal ion 'M' and metal chelate M–EDTA by polarographic method[12–15] and by spectrophotometric method.[16–17] It has been found that during the substitution reaction between the metal ion M′ and M–EDTA chelate a mixed binuclear intermediate chelate of the type M–EDTA–M′ was formed.[17–18] Kopanica[19] has suggested that the substitution reaction between calcium ion and Zn–TTHA chelate proceed through a mixed binuclear chelate which is comparitively stable.

From the review of the literature it appeared that the nature and the mechanism of the substitution reaction of metal chelates of TTHA was not studied intensively. The present work was undertaken with a view to study the mechanism and kinetics of the substitutions reactions of metal chelate of TTHA. In course of the study special attention has been given to verify the existence of the reaction intermediates and also to determine their stability constants. It has been found that under given conditions the attack of the metal ion M′ on the chelate molecule M–TTHA results in the formation of relatively stable mixed binuclear chelate M–TTHA–M′.

Experimental

Reagents. Triethylenetetraminehexaacetic acid (TTHA) is sparingly soluble in water. A 0.01 M stock solution was prepared by dissolving 2.484 g of TTHA in 13 ml of 1 M NaOH and by diluting to 500 ml with redistilled water.[10] The solution was standardized against standard zinc solution amperometrically and also by complexometric titration using Eriochrome Black T as an indicator. Solutions of 0.01 M Cu(II) and 0.01 M Ni(II) were prepared from the respective sulphate salt and were standardised against standard Na$_2$EDTA solution by amperometric titration[20–21] and also by complexometric titration against standard Na$_2$EDTA solution using murexide indicator.[22] A 0.2 M acetate buffer (pH 3.55—5.76) and 0.2 M NaClO$_4$ solution (pH 5.0—5.55) were prepared according to the known method.[23–24]

---

[1] A. E. Frost, *Nature*, **178**, 322 (1956).

[2] J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).

[3] R. Pribil and V. Vesely, *Talanta*, **9**, 939 (1962),; **10**, 899 (1963); **11**, 1319 (1964); **12**, 475, 925 (1965).

[4] T. A. Bohigian, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 832 (1967).

[5] T. A. Bohigian, Jr., and A. E. Martell, *Inorg. Chem.*, **4**, 1264 (1965).

[6] L. Harju, *Anal. Chim. Acta.*, **50**, 475 (1970).

[7] V. Linden and A. Georgio, *Helv. Chim. Acta*, **53**, 569 (1970).

[8] K. H. Schroder, *Acta. Chem. Scand.*, **20**, 881 (1966).

[9] K. S. Klausen, G. O. Kalland and E. Jacobsen,, *Anal. Chim. Acta*, **33**, 76 (1965).

[10] G. Gonradi, M. Kopanica, and J. Koryta, *Collect. Czech. Chem. Commun.*, **30**, 2029 (1965).

[11] D. N. Purohit, *J. Polarog. Soc.*, **12**, 109 (1966).

[12] N. Tanaka, K. Kato, and R. Tamamushi, This Bulletin, **31**, 283 (1958).

[13] N. Tanaka and K. Kato, *ibid.*, **32**, 1376 (1959); **33**, 1236 (1960).

[14] K. Kato, *ibid.*, **33**, 600 (1960).

[15] N. Tanaka and M. Kodama, *ibid.*, **35**, 1596 (1962).

[16] T. J. Bydalek and D. W. Margerum, *J. Amer. Chem. Soc.*, **83**, 4326 (1961).

[17] D. W. Margerum, D. L. Janes, and H. M. Rosen, *ibid.*, **87**, 4463 (1965).

[18] T. J. Bydalek, *Inorg. Chem.*, **4**, 232 (1965).

[19] M. Kopanica, *Talanta*, **15**, 1457 (1968).

[20] N. Tanaka and Y. Sakuma. This Bulletin, **32**, 578 (1959).

[21] N. Tanaka, M. Kodama, M. Sakaki, and M. Sugino, *Bunseki Kagaku*, **6**, 86 (1957).

[22] F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetate Acid," D. Van Nostrand Co., Inc., (1957), pp. 241, 234, 149.

[23] A. I. Vogel, "A Text Book of Qualitative Inorganic Analysis,." Longmans Green and Co., New York.

[24] J. Heyrovsky, "Practical Polarography," Academic Press, London and New York, p. 101.

Apparatus. *Polarographic Arrangement*: The current–voltage curves were measured with a pen-recording polarograph model LP-60. This polarograph was designed and produced by the Czechoslovak National Enterprise Laboratorni Pristroje (Laboratory Instrument) in Prague and exported through the foreign trade company KOVO of Czechoslovakia. A saturated calomel electrode of large surface area was prepared in one compartment of the Kalousek cell and used as reference electrode. The other compartment was used for electrolysis of the solution under investigation. Dropping mercury electrode (DME) was used as indicating electrode. The capillary characteristics, measured in 0.2 M KNO_3 solution at a mercury height of 60.0 cm at temperature 20 °C and at a potential −0.60 V, were $m=2.34$ mg/s and $t=3.675$ s.

Procedure. The polarographic current–voltage curves were recorded with a pen-recording polarograph as described before. Polarographic measurements were carried out in 0.2 M acetate buffer of pH 4.7 and in 0.2 M $NaClO_4$ solution of pH 5.15 at 20 °C unless it is mentioned otherwise. Gelatin was added as a maximum suppressor by 0.003% in concentration. The corrected height of the mercury reservior was kept constant at 60.0 cm. The dissolved oxygen from the sample solutions was removed by bubbling pure nitrogen gas through the solutions prior measurement.

Copper(II) and nickel(II) form Cu_2X^{2-} and Ni_2X^{2-} with TTHA (H_6X=TTHA) when copper(II) ions and nickel(II) ions react separately with TTHA. Amperometric titration of equimolar mixture of copper(II) ions and nickel(II) ions with TTHA was carried out in 0.2 M acetate buffer and 0.2 M $NaClO_4$ solution to ascertain the joint behaviour and it was observed that both copper wave and nickel wave diminished simulatneously and became zero when the molar ratio Cu: Ni: TTHA=1: 1: 1.

Exactly equimolar amounts of copper and TTHA solutions were mixed in a number of flasks containing 0.2 M $NaClO_4$ solution and then exactly equimolar amount of nickel solution was added. The ionic strength was adjusted to $\mu=0.2$ with requisite amount of concentrated $NaClO_4$ solution and the volumes of all the samples were made equal by the supporting electrolyte. Polarograms were recorded after 20 min, 24 and 72 hr and it was found that all the nickel ions added have entered into the Cu–TTHA chelate and no copper was released from the chelate. Both the above experiments indicate the formation of a stable mixed binulcear $CuXNi^{2-}$ chelate.

The effect of excess of Ni^{2+} ions on $CuXNi^{2-}$ chelate was investigated in acetate buffer and in $NaClO_4$ solution as follows. Solutions $CuXNi^{2-}$ were prepared in 12 measuring flasks and varying amount of nickel solution was added. The ionic strength was adjusted by adding concentrated $NaClO_4$ solution and the volumes of all the samples were made equal by the supporting electrolyte. The samples were kept in a thermostat at 20 °C for 72 hr and polarograms were recorded. The concentrations of released copper and unreacted nickel were measured directly from the polarograms with the help of calibration curves for copper and nickel. The effect of excess of Ni^{2+} ions on Cu_2X^{2-} was studied as above. In all cases limiting currents of free metal ions were corrected for residual current.

Potentiometric Measurement. The interaction of hexabasic TTHA acid with metal ions was studied potentiometrically. A Radiometer pH meter model PHM 4 with pH scale 0 to 14 and reproducibility of ±0.001 pH unit was calibrated so as to determine the hydrogen ion concentration directly and this was done by direct titration of standard dil. HCl with standard NaOH solution in a medium of constant ionic strength ($\mu=0.2$) maintained by KNO_3 solution. A stream of pure nitrogen gas was passed through the titration vessel and the solution was stirred with a magnetic stirrer before each measurement. The hexabasic TTHA acid was first titrated with standard NaOH solution. Since TTHA is a decadentate ligand, both 1: 1 and 2: 1 metal chelates were expected to be formed and therefore mixtures of metal and ligand of the above ratios were investigated. To ascertain the formation of mixed binuclear metal chelates Cu–X–Ni type, mixtures of Cu^{2+} ions, Ni^{2+} ions and TTHA of ratios 1: 1: 1 were titrated against standard NaOH solution.

Results

Polarographic Investigation of the Reaction between Copper(II), Nickel(II) and TTHA. Amperometric titration of Cu(II) ions and Ni(II) ions with TTHA separately showed that Cu_2X^{2-} chelate and Ni_2X^{2-} chelate were formed. An equimolar mixture of Cu(II) ions and Ni(II) ions was titrated amperometrically with TTHA in 0.2 M acetate buffer and also in 0.2 M $NaClO_4$ solution. The titration polarograms, recorded 20 hr after addition of TTHA, consist of three waves; first one due to the reduction of free copper ions, second one due to the reduction of copper from the chelate and third one due to the reduction of free nickel ions. No wave for the reduction of nickel chelate is appeared. The limiting currents of Cu(II) ions, chelate and Ni(II) ions were measured at −0.20, −0.80, and −1.25 V *vs.* SCE respectively. The height of the limiting currents of Cu(II) ions and Ni(II) ions decreased simultaneously with the addition of TTHA and the height of the chelate wave increased. The height of the waves of Cu(II) ions and Ni(II) ions became zero at the molar ratio 1: 1: 1 of Cu^{2+}, Ni^{2+}, and TTHA and only the wave of the chelate appeared (Fig. 1). The titration curves indicate that most probably a mixed binuclear $CuXNi^{2-}$ chelate is formed which is quite stable and polarographically active. An increase of concentration of TTHA beyond the above ratio shifted the half-wave potential of the chelate wave towards negative potential,

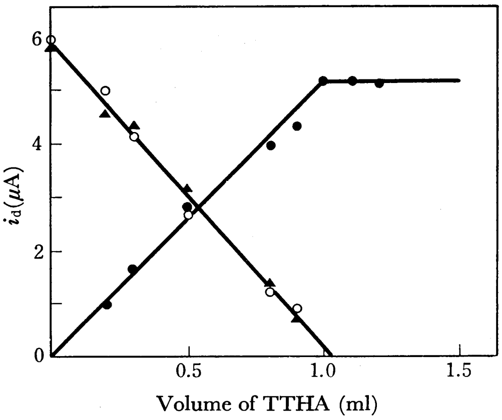

Fig. 1. Amperometric titration of a mixture of Cu(II) ions and Ni(II) ions (1: 1) with TTHA in acetate buffer of pH 4.7. Recorded 20 hr after addition. ○: wave of free copper ions, ●: wave of chelate, ▲: wave of free nickel ions.

Polarographic Behaviour of $CuXNi^{2-}$ Chelate. Polarogram recorded from solution containing Cu^{2+}, TTHA and Ni^{2+} in the molar ratio 1 : 1 : 1 in 0.2 M acetate buffer shows that only a single well-defined wave appears due to the reduction of copper from the chelate $CuXNi^{2-}$. The half-wave potential of the wave is −0.248 V *vs.* SCE. The polarographic behaviour such as the effect of (a) pressure, (b) excess TTHA, (c) temperature and (d) gelatin on the reduction wave of $CuXNi^{2-}$ chelate is similar to the corresponding behaviour of Cu_2X^{2-} chelate wave. The effect of pH on the reduction wave of $CuXNi^{2-}$ is different from its effect on the reduction wave of Cu_2X^{2-} when all other conditions are maintained constant. In case of $CuXNi^{2-}$, the second wave does not appear at higher pH as it appears in case of Cu_2X^{2-} chelate. The height of the limiting current of $CuXNi^{2-}$ remains unchanged with pH of the buffer but the half-wave potential of $CuXNi^{2-}$ wave shifted towards negative with the increase of pH. The above observations supported the proposal of the formation of a mixed binuclear $CuXNi^{2-}$ chelate.

Potentiometric Titration Studies. Potentiometric titration curves of TTHA acid in absence of metal ions and in presence of one and two moles of metal ions per mole of TTHA are presented in Fig. 2. The pH is plotted against '*a*', the number of moles of hydroxide ion added per mole of TTHA. The neutralization of the free TTHA occurs in three steps, which has a weak inflection at $a=3$ and a strong inflection at $a=4$. The first step is the reaction of the neutral form of the ligand to form a trinegative anion. The next step occurs at an '*a*' value 4 and results in the formation of tetranegative anion. The neutralization of 5th and 6th protons occurs between an '*a*' value 4 and 6 in overlapping dissociation steps.

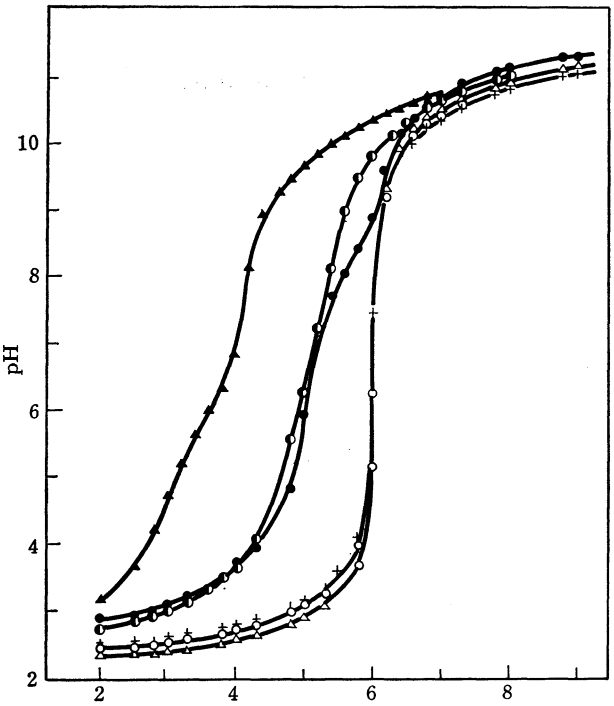

Fig. 2. Potentiometric titration of Cu(II) & Ni(II) chelates of TTHA at 20 °C in 0.20 M KNO_3 with the following molar ratios of metal ions to TTHA.
1) TTHA alone, 2) Cu: TTHA (1: 1), 3) Ni: TTHA (1: 1), 4) Cu: TTHA (2: 1), 5) Cu: Ni: TTHA (1: 1: 1), 6) Ni: TTHA (2: 1). '*a*'=mol of base added per mol of ligand. $C_{TTHA}=8.3\times10^{-4}$ M.

The titration curve of 1 : 1 Cu : TTHA consists of two inflections at an '*a*' value of 5 and 6 indicating the formation of a protonated metal chelate which dissociates at relatively higher pH value to form a normal chelate (Fig. 2). In case of 1 : 1 Ni : TTHA system the subsequent dissociation step is not as sharp as in the case of Cu : TTHA system. The reaction in case of Cu(II) : TTHA system can be represented as follows:

$$H_6X + Cu^{2+} + 5OH^- \longrightarrow CuHX^{3-} + 5H_2O,\ 5OH^-/TTHA \quad (1)$$

where H_6X represents TTHA. Since $CuHX^{3-}$ is a relatively weak acid, the second reaction step involves the neutralization of the remaining proton to form a normal chelate CuX^{4-}.

$$CuX^{3-} + OH^- \longrightarrow CuX^{4-} + H_2O,\ OH^-/TTHA \quad (2)$$

The reactions of Ni(II) occur similarly.

The titration curve of 2 : 1 Cu : TTHA indicates that the 6 protons of the ligand are neutralized in a single step at an '*a*' value of 6 and a binuclear Cu_2X^{2-} chelate is formed.

$$H_6X + 2Cu^{2+} + 6OH^- \longrightarrow Cu_2X^{2-} + 6H_2O,\ 6OH^-/TTHA \quad (3)$$

Similar titration curve is obtained when 2 : 1 Ni : TTHA is titrated. No indication of the formation of hydroxo chelate is observed at higher pH.

The titration curve of a mixture of Cu^{2+} ions, Ni^{2+} ions and TTHA of molar ratio 1 : 1 : 1 has a single inflection at an '*a*' value of 6 indicating the formation of stable mixed binuclear chelate $CuXNi^{2-}$. The reaction is represented as follows:

$$Cu^{2+} + Ni^{2+} + H_6X + 6OH^- \longrightarrow CuXNi^{2-} + 6H_2O,\ 6OH^-/TTHA \quad (4)$$

There is no subsequent hydrolysis step at higher pH and this indicates that the mixed binuclear chelate $CuXNi^{2-}$ is quite stable.

Polarographic Investigation of the Reaction between $CuXNi^{2-}$ Chelate and Nickel(II) Ions. Amperometric titration of an equimolar mixture of Cu(II) ions and Ni(II) ions with TTHA, and potentiometric titration of 1 : 1 : 1 molar ratio of Cu(II) ions, Ni(II) ions and TTHA bear the evidence of formation of a mixed binuclear $CuXNi^{2-}$ chelate over the pH range 4.7—5.15. Polarogram of $CuXNi^{2-}$ chelate is a well-defined wave ($E_{1/2}=-0.248$ V *vs.* SCE) due to the reduction of copper from the chelate. Addition of further amount of Ni(II) ions to the solution of $CuXNi^{2-}$ shows that copper is replaced by nickel from $CuXNi^{2-}$ to form binuclear Ni_2X^{2-} chelate. The exchange reaction is represented as follows:

$$CuXNi^{2-} + Ni^{2+} \rightleftharpoons Ni_2X^{2-} + Cu^{2+} \quad (5)$$

TABLE 1. STABILITY CONSTANT OF $CuXNi^{2-}$ CHELATE AT 20 °C AND IONIC STRENGTH $\mu=0.20$

Cu:X:Ni	C_{Cu} ×10⁴M	C_X ×10⁴M	C_{CuXNi} ×10⁴M	C_{Ni} ×10⁴M	Equilibrium concentration				K_{eq}	log K_{eq}	log K^{Cu}_{CuXNi}
					$[Cu^{2+}]$ ×10⁴M	$[CuXNi^{2-}]$ ×10⁴M	$[Ni_2X^{2-}]$ ×10⁴M	$[Ni^{2+}]$ ×10⁴M			
1 : 1 : 2	8.0	8.0	8.0	16.0	1.09	6.91	1.09	4.97	3.46×10^{-2}	−1.46	15.76
1 : 1 : 3	8.0	8.0	8.0	24.0	1.78	6.22	1.78	13.02	3.91×10^{-2}	−1.41	15.71
1 : 1 : 4	8.0	8.0	8.0	32.0	1.87	6.13	1.87	20.70	2.76×10^{-2}	−1.56	15.86
1 : 1 : 5	8.0	8.0	8.0	40.0	2.34	5.66	2.34	27.60	3.51×10^{-2}	−1.46	15.76
										Av.	15.77
1 : 1 : 2	8.0	8.0	8.0	16.0	1.592	6.408	1.592	5.52	7.14×10^{-2}	−1.15	15.45
1 : 1 : 3	8.0	8.0	8.0	24.0	2.682	5.318	2.682	13.27	10.18×10^{-2}	−0.99	15.29
1 : 1 : 4	8.0	8.0	8.0	32.0	3.160	4.840	3.160	19.81	10.42×10^{-2}	−0.98	15.28
1 : 1 : 5	8.0	8.0	8.0	40.0	3.740	4.260	3.740	27.90	11.76×10^{-2}	−0.93	15.23
1 : 1 : 2	4.0	4.0	4.0	8.0	1.01	2.99	1.01	3.20	10.30×10^{-2}	−0.99	15.29
1 : 1 : 3	4.0	4.0	4.0	12.0	1.63	2.37	1.36	7.33	15.30×10^{-2}	−0.82	15.12
1 : 1 : 2	12.0	12.0	12.0	24.0	2.59	9.41	2.59	9.08	7.86×10^{-2}	−1.11	15.41
1 : 1 : 3	12.0	12.0	12.0	36.0	3.90	8.10	3.90	19.60	9.60×10^{-2}	−1.004	15.30
										Av.	15.30

First set: in 0.2M acetate buffer of pH 4.70
Second set: in 0.2M $NaClO_4$ solution of pH 5.15
X=TTHA

The kinetic study of the Eq. (5) showed that the equilibrium reached within 48 hr, still to ensure completion of the reaction, the equilibrium concentrations were studied after 72 hr. The equilibrium constant K_{eq} of the reaction (5) can be defined as

$$K_{eq} = \frac{[Ni_2X^{2-}]\times[Cu^{2+}]}{[CuXNi^{2-}]\times[Ni^{2+}]} \qquad (6)$$

$$= \frac{[Ni_2X^{2-}]}{[NiX^{4-}]\times[Ni^{2+}]} \times \frac{[Cu^{2+}]\times[NiX^{4-}]}{[CuXNi^{2-}]}$$

$$= K^{Ni}_{Ni_2X}\cdot K^{Cu}_{CuXNi} \qquad (6a)$$

where

$$NiX^{4-} + Ni^{2+} = Ni_2X^{2-},$$

$$K^{Ni}_{Ni_2X} = \frac{[Ni_2X^{2-}]}{[NiX^{4-}]\times[Ni^{2+}]} \qquad (7)$$

and

$$CuXNi^{2-} = Cu^{2+} + NiX^{4-},$$

$$K^{Cu}_{CuXNi} = \frac{[Cu^{2+}]\times[NiX^{4-}]}{[CuXNi^{2-}]} \qquad (8)$$

The determination of the equilibrium constant K_{eq} leads directly to the determination of the stability (formation) constant of $CuXNi^{2-}$ which is related to K_{eq} by Eq. (6a). The Eq. (7) represents formation constant of Ni_2X^{2-} and Eq. (8) represents the dissociation constant of $CuXNi^{2-}$ and its reciprocal is the stability (formation) constant K^{Cu}_{CuXNi} of $CuXNi^{2-}$-chelate.

In equilibrium state, the concentrations of released copper ions and unreacted nickel ions are measured from the polarograms by means of calibration curves. As the metal ions and the metal chelates are not hydrolysed at the pH used, the concentrations of other species in the equilibrium state were calculated according to the method of M. Kopanica[19] and can be given by

$$[CuXNi^{2-}] = C_{Cu} - [Cu^{2+}] \qquad (9)$$

$$[Ni_2X^{2-}] = C_X - [CuXNi^{2-}] = C_X - C_{Cu} + [Cu^{2+}] \qquad (10)$$

where C_{Cu}, C_X represent the total concentration of copper and the ligand respectively. Substituting the value of $[Cu^{2+}]$, $[Ni^{2+}]$, $[CuXNi^{2-}]$, and $[Ni_2X^{2-}]$ into Eq. (6) gives the Eq. (11)

$$K_{eq} = \frac{[Cu^{2+}]^2}{\{C_{Cu}-[Cu^{2+}]\}[Ni^{2+}]} \qquad (11)$$

The equilibrium constant K_{eq} is calculated with the help of Eq. (11). When K_{eq} is substituted into Eq. (6a) and the reciprocal of dissociation constant is taken as stability constant of $CuXNi^{2-}$, then the Eq. (6a) is reduced to Eq. (12).

$$K^{Cu}_{CuXNi} = \frac{K^{Ni}_{Ni_2X}}{K_{eq}} \qquad (12)$$

The formation constant $K^{Ni}_{Ni_2X}$ is known[25] and hence K^{Cu}_{CuXNi} is calculated from Eq. (12) and the values of log K^{Cu}_{CuXNi} are presented in Table 1.

Reaction between Cu_2X^{2-} Chelate and Ni(II) Ions. Amperometric titration and potentiometric titration results showed that Cu_2X^{2-} chelate is formed in acetate buffer and $NaClO_4$ solution when copper ions and TTHA are present in the molar ratio 2: 1. When excess of Ni(II) ions are added to the solution of Cu_2X^{2-}, copper is released from the chelate and Ni_2X^{2-} is formed. At higher concentration of Ni^{2+}, the exchange reaction takes place directly without the formation of mixed intermediate binuclear chelate. The exchange reaction is expressed as follows:

$$Cu_2X^{2-} + 2Ni^{2+} \rightleftharpoons Ni_2X^{2-} + 2Cu^{2+} \qquad (13)$$

The equilibrium constant K_{eq} of the reaction (13) is represented by

$$K_{eq} = \frac{[Ni_2X^{2-}]\times[Cu^{2+}]^2}{[Ni^{2+}]^2\times[Cu_2X^{2-}]} \qquad (14)$$

$$= \frac{[Ni_2X^{2-}]}{[Ni^{2+}]^2\times[X^{6-}]} \times \frac{[Cu^{2+}]^2\times[X^{6-}]}{[Cu_2X^{2-}]} = \frac{K_{Ni_2X}}{K_{Cu_2X}} \qquad (14a)$$

where K_{Ni_2X} and K_{Cu_2X} are the formation constants of Ni_2X^{2-} and Cu_2X^{2-} respectively. The Eq. (13) is studied in 0.2 M $NaClO_4$ of pH 5.15 and the equi-

---

[25] L. Harju and A. Ringbom, *Anal. Chim. Acta*, **49**, 221 (1970).

TABLE 2. STABILITY CONSTANT OF Cu_2X^{2-} CHELATE AT 20 °C AND IONIC STRENGTH $\mu=0.2$. 0.2M $NaClO_4$ SOLUTION OF pH 5.15 IS USED AS SUPPORTING ELECTROLYTE. X=TTHA

Cu:X:Ni	C_{Cu} ×10⁴M	C_X ×10⁴M	C_{Ni} ×10⁴M	Equilibrium concentration				K_{eq}	logK_{eq}	log K_{Cu_2X}
				$[Cu^{2+}]$ ×10⁴M	$[Cu_2X^2]$ ×10⁴M	$[Ni^{2+}]$ ×10⁴M	$[Ni_2X^{2-}]$ ×10⁴M			
2 : 1 : 4	4.0	2.0	8.0	2.36	0.82	6.38	0.81	1.37×10^{-1}	−0.863	33.26
2 : 1 : 8	4.0	2.0	16.0	2.87	0.565	14.85	0.575	0.38×10^{-1}	−1.42	33.82
2 : 1 : 4	8.0	4.0	16.0	4.59	1.71	12.37	1.82	1.47×10^{-1}	−0.83	33.23
2 : 1 : 8	8.0	4.0	32.0	5.88	1.06	28.50	1.75	0.703×10^{-1}	−1.15	33.55
2 : 1 : 4	12.0	6.0	24.0	6.80	2.60	18.30	2.85	1.54×10^{-1}	−0.813	33.21
2 : 1 : 8	12.0	6.0	48.0	8.64	1.68	43.30	2.35	0.557×10^{-1}	−1.25	33.65
										Av. 33.45

librium concentrations of released copper ions and unreacted nickel ions are measured polarographically 72 hr after mixing. The total concentrations of Cu^{2+}, Ni^{2+} and TTHA are known, the concentrations of Cu_2X^{2-} and Ni_2X^{2-} are calculated and hence the value of K_{eq} is calculated from Eq. (14). The formation constant K_{Ni_2X} is known[25] and hence the formation (stability) constant K_{Cu_2X} of Cu_2X^{2-} is calculated from Eq. (14a) and the values of log K_{Cu_2X} are presented in Table 2.

Discussion

During the study of the substitution reactions between Cu–TTHA chelate and nickel ions, the existence of the mixed binuclear chelate $CuXNi^{2-}$ is established. This has been done by amperometric titration of equimolar mixture of Cu^{2+} ions and Ni^{2+} ions with TTHA. Figure 1 shows the simultaneous decrease of free Cu^{2+} ions and free Ni^{2+} ions waves during the addition of TTHA while new wave appeared which is not the wave of Cu_2X^{2-} chelate ($E_{1/2CuXNi}=-0.248$ V, $E_{1/2Cu_2X}=-0.240$ V *vs.* SCE). Section of polarographic behaviour of $CuXNi^{2-}$ chelate is a summary of proofs that the new wave observed does not correspond to the wave of Cu_2X^{2-} chelate. Further evidence of the existence of the mixed binuclear chelate $CuXNi^{2-}$ is the quantitative treatment of the system containing Cu^{2+} ions, Ni^{2+} ions and TTHA ligand. The polarographic measurement enables to collect the data of the concentrations of free Cu^{2+} ions and Ni^{2+} ions which are used for the calculation of the formation constant K^{Cu}_{CuXNi}, the log value of which is 15.30. This constant value calculated under different concentration conditions (Table 1) verifies the proposal of mixed binuclear chelate formation. Further verification of the system of calculation and the accuracy of the experimental data is done by the determination of the stability constant of Cu_2X^{2-} chelate based on the substitution reaction between Cu_2X^{2-} chelate and Ni^{2+} ions (Table 2). The agreement of the obtained value of the stability constant K_{Cu_2X} with the literature value[25] is satisfactory.

Finally the existence of the mixed binuclear chelate $CuXNi^{2-}$ is verified by potentiometric study of neutralization of the mixture of Cu^{2+} ions, Ni^{2+} ions and TTHA ligand (Fig. 2).

Comparison of the results obtained by the polarographic study of the substitution reaction of Cu-chelate with Ni^{2+} ions led to the following conclusion. In the reaction between CuY^{2-} (H_4Y=EDTA) and Ni^{2+} ions the mixed binuclear chelate CuYNi exists only as an intermediate state. During the polarographic examination of the substitution reaction $CuY^{2-}+Ni^{2+}$ (1 : 1) it has been found that in equilibrium state, which comes after 24 hr of mixing, the concentration of free Ni^{2+} ions is equal to the concentration of CuY^{2-} chelate. At the beginning of the reaction the concentration of CuY^{2-} chelate is higher than that of free Ni^{2+} ions. This indicates that at the beginning of the reaction Ni^{2+} ions enter into the CuY^{2-} chelate to form the intermediate CuYNi chelate of sufficient concentration which gradually dissociates to Cu^{2+} and NiY^{2-} chelate. When the substitution reaction of DTPA chelate is studied the formation of mixed binuclear chelate $CuZNi^{-}$ (H_5Z=DTPA) is established and the stability constant of this chelate is determined.[26] In the case of substitution reaction of TTHA chelate the formation of the mixed binuclear chelate is again established. From the above results it is evident that the stability of the mixed binuclear chelate increases with the increase of the number of the donor groups in the ligand molecule.

---

[26] M. S. Haque and M. Kopanica, "Polarographic Study of the Substitution Reactions between Metal Ions and Copper Chelates of Diethylenetriaminepentaacetic Acid," Indian Journal of Applied Chemistry. (Submitted for publication).