A POLAROGRAPHIC STUDY OF THE SUBSTITUTION REACTIONS OF THE CHELATES OF TRIETHYLENETETRAMINEHEXAACETIC ACID. III.*

THE REACTION OF INDIUM CHELATES

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The reactions between indium triethylenetetraminehexaacetate (TTHA) chelates and nickel(II) or gallium(III) ions were examined using polarographic technique. It has been found that mixed binuclear chelates of the type In-Ni-TTHA or In-Ga-TTHA were formed. These chelates yield polarographic waves which, in some cases, can be used for the evaluation of the concentration stability constant of the mixed binuclear chelate.

In the earlier papers[1-3], the mechanism of the substitution reactions involving the chelates of triethylenetetraminehexaacetic acid (TTHA or H_6X) with divalent metal ions was examined and the existence of mixed binuclear chelates[3] was verified. In the present work are summarized the results of a similar study connected with the reactions of the TTHA chelates of trivalent metal ions.

EXPERIMENTAL

Reagents and Apparatus. All the solutions used were prepared from reagent grade chemicals. The solutions of metal salts were standardized by visual and amperometric titrations with EDTA using the recommended procedures. The TTHA solution ($0{\cdot}01$ mol l^{-1}) was prepared from the reagent of Geigy Chemical Co., Basel, Switzerland and standardized by titration with a standard zinc solution[4]. Essentially identical instrumentation (polarograph, pH meter) was used as described in the previous paper[5].

RESULTS AND DISCUSSION

THE SYSTEM CONTAINING INDIUM(III), NICKEL(II) IONS AND TTHA REAGENT

Preliminary Experiments

The TTHA reagent was found[5] to form a polarographically active binuclear chelate with indium(III) ions. This chelate yields a wave at pH values above 2·7; the value of the corresponding half wave potential is 0·74 V (S.C.E) at pH 3·6. No wave for the indium TTHA chelate appears

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in the pH range below 2·7 (ref.[5]). This finding enables the amperometric titration of indium with TTHA at pH values below 2·7, where the parameter followed is the height of the wave of free indium(III) ions. Under identical conditions nickel was also titrated with TTHA; for end-point indication, the heights of the polarographic waves of uncomplexed nickel(II) ions were measured. The results of such titrations agree very well with the theory; some unusual phenomena were, however, observed when mixtures of indium(III) and nickel(II) ions were titrated with TTHA. Because establishment of the corresponding equilibrium is slow the "titration" experiments were carried out as follows: a series of solutions was prepared containing a constant amount of indium and nickel and varying amounts of the reagent; the polarograms of uncomplexed indium(III) and nickel(II) ions were recorded after a given time interval. From the thus obtained data a diagram was constructed showing the variation of the concentration of uncomplexed indium(III) and nickel(II) ions in dependence on the amount of the reagent added. As follows from Fig. 1 the concentration of free nickel(II) and indium(III) ions decreases with an increasing amount of TTHA in the system examined. During these experiments it was observed that a new wave appeared on the polarogram (Fig. 1, curve *3*); this wave did not correspond to the previously described wave of the binuclear indium TTHA chelate[5]. All the observed waves (*i.e.* the waves of uncomplexed indium(III) and nickel(II) ions and the new wave with more negative half-wave potential) disappeared when the system contained amounts of the TTHA reagent corresponding to the formation of 1 : 1 indium and 2 : 1 nickel TTHA chelates. This result was verified by measurements carried out with solutions containing various indium : nickel molar ratios. The height of the new wave, with a half-wave potential equal to −0·76 V (S.C.E.), was found to depend on the composition of the system studied. The height of this wave passed through a maximum value and was minimum at the point corresponding to complete complexation of indium and nickel (the formation of 1 : 1 indium and 2 : 1 nickel TTHA chelates).

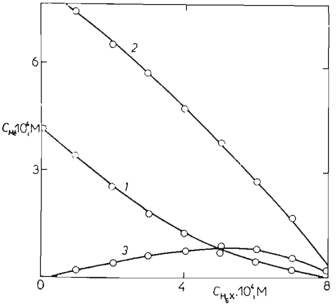

FIG. 1

The Variation of the In(III) and Ni(II) Ion Concentrations in Dependence on the Amount of TTHA Reagent

$C_{In} = 4 . 10^{-4}$M; $C_{Ni} = 8 . 10^{-4}$M pH 2·4; 50 h after mixing. Variation of concentrations: *1* In (III) ion; *2* Ni(II) ion; *3* of the mixed chelate.

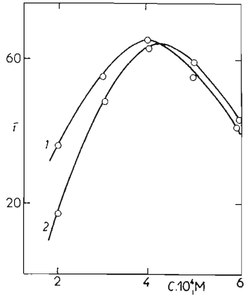

FIG. 2

Dependence of the Height of the Wave of the Mixed Chelate $InNiX^-$ on the Composition of the System

1 $C_{In} = C_{Ni} = 4 . 10^{-4}$M; C_X varies from $2 . 10^{-4}$M to $6 . 10^{-4}$M; pH 2·4. *2* $C_{Ni} = C_X = 4 . 10^{-4}$M; C_{In} varies from $2 . 10^{-4}$M to $6 . 10^{-4}$M; pH 2·4. $\bar{\imath}$ arbitrary units (mm).

The measurements of the time dependences of the heights of all observed waves in the system studied have shown that the sum of the heights of the wave of free indium(III) ions and the "new" wave is constant, the height of the wave of free indium(III) ions increasing with time and the height of the "new" wave decreasing with time. The equilibrium state was established approx. 50 h after mixing the components.

On the basis of preliminary experiments, the following proposal was made; immediately after mixing of all components the binuclear mixed chelate $InXNi^-$ is formed which slowly enters the equilibrium shown by the reaction

$$InXNi^- \rightleftarrows 0{\cdot}5\,In^{3+} + 0{\cdot}5\,Ni_2X^{2-} + 0{\cdot}5\,InX^{3-}\,. \qquad (A)$$

The appearance of the second, more negative wave, was proposed to be due to the reduction of indium from the mixed binuclear chelate. The maximum height of the wave corresponding to the binuclear chelate was found under conditions where the total concentrations of indium(III) and of nickel(II) ions and of the reagent were equal. The variations of the heights of the described wave in dependence or the composition of the system examined are summarized in Fig. 2.

The half-wave potentials of the waves of the binuclear and mixed binuclear indium TTHA chelates are identical and cannot be experimentally distinguished. To show that the wave described in this study corresponds to the reduction of indium from the mixed binuclear chelate, the following findings should be taken into account: *1*. In solutions with a 1 : 1 : 1 molar ratio mixture of TTHA : nickel : indium, the height of the wave of free nickel(II) ions does not correspond to the presence of only simple TTHA chelates of both metals. *2*. As described in the previous paper[5], the temperature coefficient corresponding to the wave of In_2X chelate has the value 0·85%/°C; the value of this coefficient corresponding to the wave of the mixed binuclear chelate was found to be 1·25%/°C in the temperature range 20–50°C. *3*. The heights of both studied waves depend linearly on the concentration of the In_2X and $InNiX^-$ chelates respectivelly. *4*. The dependences of the wave heights on the square roots of the heights of the mercury reservoir are linear in both cases. In the case of the mixed binuclear chelate this dependence passes through the origin; in the case of the In_2X chelate this was not observed. *5*. As shown in Fig. 3, the pH dependences of the wave heights of the In_2X chelate and of the mixed binuclear chelate differ significantly.

These facts together with the shape of the curves in Fig. 2 (maximum height of the wave corresponds to the system with the composition TTHA : In : Ni = 1 : 1 : 1) support the proposal that the described wave corresponds to the reduction of the mixed binuclear chelate.

Calculation of the Stability Constant of the InNiX *Chelate*

It can be supposed that the mixed binuclear chelate $InNiX^-$ is formed according to the reaction

$$In^{3+} + NiX^{4-} \rightleftarrows InNiX^- \qquad (B)$$

and the corresponding stability constant K^{In}_{InNiX} is defined by the expression

$$K^{In}_{InNiX} = [InNiX^-]/[In^{3+}][NiX^{4-}]. \quad (1)$$

The value of the constant K^{In}_{InXNi} was calculated using the polarographically determined concentration of free indium(III) ions (*a*) of the mixed binuclear chelate (*b*) and of the free nickel(II) ions (*c*). The total concentration of nickel C_{Ni} was defined by the equation

$$C_{Ni} = [Ni^{2+}] + [InNiX^-] + 2[Ni_2X^{2-}] + [NiX^{4-}] \quad (2)$$

and the stability constant $K^{Ni}_{Ni_2X}$ of the Ni_2X^{2-} chelate was defined as

$$K^{Ni}_{Ni_2X} = [Ni_2X^{2-}]/[NiX^{4-}][Ni^{2+}]. \quad (3)$$

When the term $[Ni_2X^{2-}]$ was expressed by equation (*3*) and inserted into equation (*2*), the following expression was obtained

$$NiX^{4-} = [C_{Ni} - (b + c)]/c(1 + 2K^{Ni}_{Ni_2X}). \quad (4)$$

Because the value of the constant $K^{Ni}_{Ni_2X}$ has been determined as approx. 10^{10} and the concentration of free nickel(II) ions (*c*) under the experimental conditions was approx. 10^{-4}M, the expression (*5*) is valid:

$$c(1 + 2K^{Ni}_{Ni_2X}) \doteq 2K^{Ni}_{Ni_2X} \cdot c. \quad (5)$$

Substitution of expression (*4*) into equation (*1*) leads to the equation

$$K^{In}_{InNiX} = 2K^{Ni}_{Ni_2X} \cdot b \cdot c/a[C_{Ni}-(b + c)], \quad (6)$$

which can be used for the calculation of the value of the constant K^{In}_{InNiX}. Values of the

TABLE I

Values of the Constant K^{In}_{InNiX} Calculated according to Eq. (*6*)
pH 2·4; total TTHA concentration $5{\cdot}0 \cdot 10^{-4}$ mol l^{-1}.

$C_{In} \cdot 10^4$ mol l^{-1}	$C_{Ni} \cdot 10^4$ mol l^{-1}	$K^{In}_{InNiX} \cdot 10^{11}$	$C_{In} \cdot 10^4$ mol l^{-1}	$C_{Ni} \cdot 10^4$ mol l^{-1}	$K^{In}_{InNiX} \cdot 10^{11}$
	Type A			Type B	
5·0	6·0	1·81	3·0	14·0	1·80
5·0	8·0	1·80	4·0	10·0	1·74
5·0	10·0	1·95	5·0	10·0	1·97
5·0	12·0	1·86			
5·0	14·0	1·72			

constant K^{In}_{InNiX} calculated on the basis of the polarographic data obtained with systems containing various amounts of both metal ions and the reagent are summarized in Table I. The mean value of the constant K^{In}_{InXNi} was found to be $1\cdot80 \cdot 10^{11}$.

In the derivation of the equation (*6*), the formation of the binuclear indium TTHA chelate was not supposed. This proposal is based on the fact that the formation of 2 : 1 indium TTHA chelate is negligible in the solutions of pH lower[5] than 2·7. Experimental data necessary for the calculation of the constant K^{In}_{InNiX} were obtained in two different ways. First, the solution of nickel salt was added to the mixture containing indium and TTHA in 1 : 1 molar ratio (A in Table I). In the second series, a solution of indium salt was added to the mixture containing nickel and TTHA in 2 : 1 molar ratio (B in Table I). The first set of measurements corresponded to the reaction

$$InX^{3-} + Ni^{2+} \rightleftarrows InNiX^{-} \qquad (C)$$

and the second set to the reaction

$$Ni_2X^{2-} + In^{3+} \rightleftarrows InNiX^{-} + Ni^{2+} . \qquad (D)$$

The agreement of the calculated results for both these reactions confirmed the proposed formation of the binuclear mixed chelate. The high stability of the mixed binuclear chelate $InNiX^{-}$ suggests the possibility of the existence of this complex even in the presence of nickel(II) ions (reaction (*D*)).

THE SYSTEM CONTAINING INDIUM(III), GALLIUM(III) IONS AND TTHA REAGENT

Gallium(III), similar to nickel(II), forms mono- and binuclear chelates with TTHA (ref.[6,7]); these chelates and gallium(III) itself are polarographically inactive. Polarographic measurements have shown that solutions containing indium(III) and gallium(III) ions and TTHA yielded a new wave which did not correspond to the reduction of any of the indium-TTHA chelates. Similarly to the previous case, it was proposed that the new wave corresponds to the reduction of the mixed chelate InGaX. The possibility of the formation of the InGaX chelate was suggested by Vydra and Vorlíček[8] on the basis of the results of biamperometric titrations of the mixtures of indium(III) and gallium(III) with TTHA reagent. The shape of the new wave and its half-wave potential was found to be identical with that of the mixed binuclear chelate $InNiX^{-}$. The dependence of the height of this "new" wave on the concentration of the proposed mixed chelate InGaX (*i.e.* the dependence of the wave height on the amount of the 1 : 1 : 1 molar mixture of indium, gallium and of the reagent in the studied solution) was linear as was the dependence of this wave height on the square root of the height of the mercury reservoir. The temperature coefficient of this wave was very close to that of the wave of InNiX chelate, the corresponding value was found to be 1·20%/°C.

Using the same technique as described in the previous section, the variation of the concentration of free indium(III) ions during the titration of the mixture of gallium and indium with TTHA reagent was determined and the corresponding results are summarized in Fig. 4. Curve 2 in Fig. 4 shows the variation of the height of the new wave in dependence on the amount of TTHA reagent added. Fig. 4 illustrates that the maximum height of the new wave was reached at the point corresponding to the

1 : 1 : 1 molar ratio mixture of both metal ions and of the reagent and that zero height was obtained when the system studied corresponded to 1 : 1 : 2 molar ratio mixture, In : Ga : TTHA. The described results led to the proposal that, during the titration, the following reactions proceeded simultaneously

$$In^{3+} + Ga^{3+} + X^{6-} \rightleftarrows InGaX\,, \qquad (E)$$

$$InGaX + X^{6-} \rightleftarrows InX^{3-} + GaX^{3-}\,. \qquad (F)$$

Further, the influence of gallium(III) ions on the In-TTHA chelates was examined. A graph, showing the dependence of the concentration of noncomplexed indium(III) ions, and of the concentration of the proposed mixed chelate InGaX, on the amount of gallium added to the system containing a 1 : 1 molar mixture of indium and TTHA, is presented in Fig. 5. The data, used for the construction of the curves in Fig. 5, were obtained by the polarographic determination of the concentration of indium(III) ions and of the mixed binuclear chelate InGaX in solutions containing constant concentrations of indium and TTHA and a varied gallium concentration. Measurements were carried out under equilibrium conditions – 50 h after mixing. If the variations

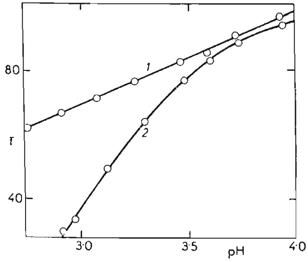

FIG. 3

pH Dependence of the Heights of the Waves of In_2X Chelate and of $InNiX^-$ Chelate

Dependence of the wave of *1* $InNiX^-$ chelate, $C_{In} = C_X = C_{Ni} = 1 \cdot 10^{-4}$M; 2 In_2X chelate, $C_{In} = 1 \cdot 10^{-4}$M; $C_X = 5 \cdot 10^{-5}$M. *i* arbitraty units (mm).

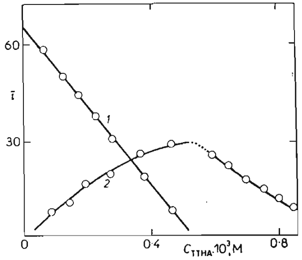

FIG. 4

Variations of the Heights of the Wave of In(III)Ions during the Amperometric Titration of the Mixture of In(III) and Ga(III) Ions with TTHA

Titration of 1 : 1 molar mixture In + Ga with TTHA reagent: *1* decrease of the In(III) ion concentration; 2 variation of the height of the wave of the binuclear mixed chelate. Monochloroacetate buffer, pH 2·7. *i* arbitrary units (mm).

of the concentrations of the components of the Ga–In–TTHA system were followed in the dependence on time, it was found that at the pH value 2·4 the concentration of free indium(III) ions increased with time while the concentration of the mixed binuclear chelate decreased with time. The system reached equilibrium after approx. 40 h. During this time period the half-wave potential of the wave of the mixed binuclear chelate remained unchanged. The observed time dependences can be interpreted as follows: In the 1 : 1 : 1 molar mixture of the reagent, indium(III), and gallium(III) ions, the mixed binuclear chelate is formed immediately; this chelate slowly forms the equilibrium mixture shown by the reaction:

$$In^{3+} + Ga^{3+} + X^{6-} \xrightarrow{\text{fast}} InGaX \rightleftarrows In^{3+} + GaX^{3-} . \qquad (G)$$

When, on the other hand, the system studied contained the chelate InX^{3-}, then after the addition of gallium(III) ions, the mixed binuclear chelate InGaX was initially formed, and further reacted as shown by reaction (*G*). The described findings verified the proposal of the existence of the mixed binuclear chelate InGaX, which exhibited the polarographic wave. Due to the lack of experimental data (impossibility of polarographic determination of the concentration of free gallium(III) ions) a quantitative treatment, similar to that described in connection with the system In–Ni–TTHA, was not done.

Similar experiments as described in this section were carried out with those systems where gallium(III) ions were replaced by another divalent metal ion (zinc, cadmium, manganese, *etc.*). In all cases similar effects were observed as are described throughout this work; the heights of the second wave were, however, too small to allow exact polarographic measurements and quantitative treatment of the obtained data.

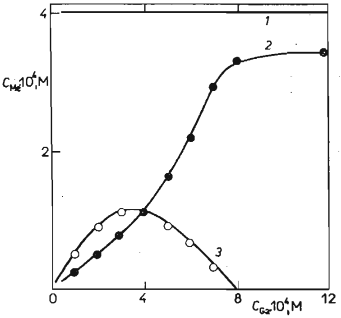

FIG. 5

Variation of the Concentration of In(III) Ions and Mixed Binuclear Chelate InGaX on the Amount of Ga

$C_{In} = C_X = 4 . 10^{-4}$M; pH 2·4; 50 h after mixing. *1* Total In concentration; *2* variation of the In(III) ion concentration; *3* variation of the concentration of the InGaX chelate.

The existence of various mixed binuclear chelates of TTHA has already been demonstrated[2,3,9]. The appearance of the "new" wave was, however, not observed in every system where the mixed binuclear chelate was formed. The lack of experimental data makes it impossible to explain generally why some mixed binuclear chelates of TTHA are polarographically active and some polarographically inactive. On the basis of the known facts one proposal seems to be acceptable: when the mixed "binuclear chelate" is formed by replacing one metal atom in the molecule of the binuclear chelate by another metal then the "new" wave appears in cases where the simple binuclear chelate is polarographically active and where the second metal ion, necessary for the formation of the mixed binuclear chelate, forms a sufficiently stabile mononuclear TTHA chelate. These conditions are fulfilled in the formation of the mixed chelates of $InNiX^-$, InGaX or $CuNiX^{2-}$ but not in the formation of $ZnNiX^{2-}$.

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