

POLAROGRAPHY OF INDIUM TRIETHYLENETETRAMINEHEXAACETATE CHELATES

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Indium(III) ions form with triethylenetetraminehexaacetic acid (TTHA) chelates with metal to ligand ratio 1 : 1 and 2 : 1. The 1 : 1 chelate is polarographically inactive while the binuclear chelate yields a polarographic reduction wave. A method was proposed for the determination of the ratio of the stability constants of both indium chelates, based on the measurement of the limiting currents of the waves of indium(III) ions and 2 : 1 indium-TTHA chelate. Using the substitution reaction between 2 : 1 nickel-TTHA chelate and indium(III) ions, the stability constant of 1 : 1 indium-TTHA chelate was determined: $\log K_{\text{InX}} = 26.53$. The stability constant of 2 : 1 indium-TTHA chelate ($\log K_{\text{In}_2\text{X}} = 30.11$) was determined from the known ratio $K_{\text{InX}} : K_{\text{In}_2\text{X}}$ and from the previously determined value of K_{InX} .

Polarographic behaviour of the chelates of triethylenetetraminehexaacetic acid (TTHA or H_6X) was investigated by various authors¹⁻³; their works involved mostly the behaviour of the chelates of divalent metal ions and only few data connected with the polarographic reduction of iron(III) TTHA chelate⁴ are known up to now. Recently Yiangst and Martell⁵ reported the results of the potentiometric study dealing with the interactions of TTHA reagent with some trivalent metal ions.

In this paper are presented the results of the study of the polarographic behaviour of indium-TTHA chelates and the stability constants of 1 : 1 and 2 : 1 metal to ligand indium chelates are reported. Stability constant of 1 : 1 indium chelate was determined on the basis of the study of the substitution reaction between 2 : 1 nickel-TTHA chelate and indium(III) ions. The ratio of the stability constants of 1 : 1 and 2 : 1 chelates was determined from the data obtained by the measurement of the limiting currents of the waves of indium(III) ions and In_2X chelate.

EXPERIMENTAL

Apparatus

Polarograms were recorded with the polarograph LP-60 (Laboratorní přístroje, Prague), using a H-type polarographic cell with a separate saturated calomel electrode. The temperature of the polarographed solutions was kept constant at 22°C using a thermostat. pH of the solutions examined was measured with a glass electrode and the pH-meter PH 25 (Radiometer, Copenhagen, Denmark).

Reagents

Triethylenetetraminehexaacetic acid used was the product of Dojin Pharmaceutical Laboratories, Japan. The purity of this reagent was tested by nitrogen, carbon and hydrogen analysis. TTHA solutions were standardized by visual⁶ and amperometric⁷ titrations with standard zinc solutions. All other chemicals used were of analytical grade.

RESULTS AND DISCUSSION

Polarography of Indium(III) ions in the Presence of TTHA

Polarographic reduction of indium(III) ions in the presence of TTHA reagent was examined in buffered and unbuffered solutions in the pH interval from 1 to 5. When the molar ratio TTHA : indium was equal to or higher than one, no polarographic wave was observed in the pH range studied. If the molar ratio TTHA : indium was lower than one and the pH value lower than 2.7, only the wave corresponding to the reduction of noncomplexed indium ions was found. If the pH value of the solution examined was higher than 2.7 and the ratio TTHA : indium lower than one, two waves appeared: the first one corresponding to the reduction of noncomplexed indium(III) ions and the second one (with more negative half-wave potential) due to the reduction of unknown species.

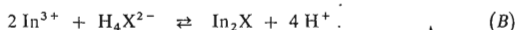
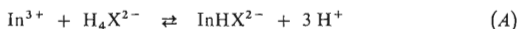
The values of limiting currents of the first and second waves corresponding to various values of the molar ratio TTHA : indium and to two different pH values are presented in Fig. 1. According to Fig. 1 it is evident that the sum of the limiting currents of both waves decreases linearly with increasing value of the ratio TTHA : indium and at the ratio TTHA : indium = 1, the sum is zero. The current of the wave corresponding to the reduction of noncomplexed indium(III) ions decreases nonlinearly with increasing value of the ratio TTHA : indium and when this ratio is equal to one, the limiting current has zero value. The limiting current of the second wave varies with varied value of the ratio TTHA : indium, its maximum value corresponding to the ratio TTHA : indium = 0.5.

It has been verified that the first wave corresponds to an irreversible electrode process (reduction of indium(III) ions) and that the current is diffusion controlled. The analysis of the more negative wave has shown that the corresponding limiting

current depends linearly on the amount of 2 : 1 indium to TTHA molar ratio mixture in the polarographed solution and that the temperature coefficient is less than one in the range 20–50°C.

The above given findings have led to the proposal that indium(III) ions form 1 : 1 and 2 : 1 metal to ligand chelates with TTHA and that the first chelate is polarographically inactive, while the second one yields a polarographic wave (the wave with more negative half-wave potential). When this proposal is valid, the following reactions and equations should hold:

Formation of both indium-TTHA chelates at pH 4 can be expressed by the reactions (A) and (B)



At the pH value 4 the prevailing form of the ligand is the protonated species H_4X^{2-} , as follows from the values of dissociation constants of TTHA^{8,9}. The proton dissociation constants $K_{\text{InHX}}^{\text{H}}$ of InHX^{2-} chelate was defined as

$$K_{\text{InHX}}^{\text{H}} = [\text{InX}^{3-}][\text{H}^+]/[\text{InHX}^{2-}] \quad (1)$$

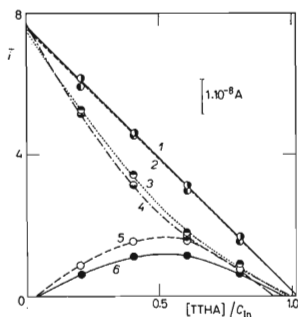


FIG. 1

Dependence of the Limiting Currents of First and Second Indium Wave on the Ratio TTHA : Indium

Supporting electrolyte 0.1M-NaClO₄, pH adjusted with buffer solution formic acid-sodium formate. $C_{\text{In}} = 4 \cdot 10^{-4}\text{M}$, 25°C; 1 sum of both limiting currents, pH 4.1; 2 as 1, pH 3.6; 3 limiting current of the wave of indium(III) ions, pH 3.6; 4 as 3, pH 4.1; 5 limiting current of the second wave, pH 4.1; 6 as 5, pH 3.6.

and the equilibrium constant of reaction (A) was defined as

$$\begin{aligned} K_1 &= [\text{InHX}^{2-}] [\text{H}^+]^3 / [\text{In}^{3+}] [\text{H}_4\text{X}^{2-}] = \\ &= [\text{InX}^{3-}] [\text{H}^+]^4 / [\text{In}^{3+}] [\text{H}_4\text{X}^{2-}] K_{\text{InHX}}^{\text{H}}. \end{aligned} \quad (2)$$

When the concentration of H_4X^{2-} species was expressed with the use of the dissociation constant $K_1, K_2, K_3,$ and K_4 of TTHA

$$[\text{H}_4\text{X}^{2-}] = [\text{X}^{6-}] [\text{H}^+]^4 / K_1 K_2 K_3 K_4 = [\text{X}^{6-}] [\text{H}^+]^4 / A, \quad (3)$$

where

$$A = K_1 K_2 K_3 K_4, \quad (3a)$$

equation (2) simplifies:

$$K_1 = [\text{InX}^{3-}] A / [\text{In}^{3+}] [\text{X}^{6-}] K_{\text{InHX}}^{\text{H}} = K_{\text{InX}}^{\text{H}} A / K_{\text{InHX}}^{\text{H}}, \quad (4)$$

where K_{InX} is the stability constant of the InX^{3-} chelate defined by the equation

$$K_{\text{InX}} = [\text{InX}^{3-}] / [\text{In}^{3+}] [\text{X}^{6-}]. \quad (5)$$

In equations (3) and (4) the concentration of the species H_5X^- and H_6X were neglected because the experimental data corresponded to the solutions of pH 3.5–4.1.

The equilibrium constant K_{II} of the reaction (B) was expressed similarly as in the previous case

$$\begin{aligned} K_{\text{II}} &= [\text{In}_2\text{X}] [\text{H}^+]^4 / [\text{In}^{3+}] [\text{H}_4\text{X}^{2-}] = \\ &= [\text{In}_2\text{X}] A / [\text{In}^{3+}]^2 [\text{X}^{6-}] = K_{\text{In}_2\text{X}} A, \end{aligned} \quad (6)$$

where $K_{\text{In}_2\text{X}}$ is the stability constant of the In_2X chelate defined by the equation

$$K_{\text{In}_2\text{X}} = [\text{In}_2\text{X}] / [\text{In}^{3+}]^2 [\text{X}^{6-}]. \quad (7)$$

The ratio of the equilibrium constants K_1 and K_{II} is given by the equation

$$K_1 / K_{\text{II}} = K_{\text{InX}} / K_{\text{In}_2\text{X}} K_{\text{InHX}}^{\text{H}} = [\text{InX}^{3-}] [\text{In}^{3+}] / [\text{In}_2\text{X}] K_{\text{InHX}}^{\text{H}}. \quad (8)$$

According to equation (8) the ratio of the constants K_{InX} and $K_{\text{In}_2\text{X}}$ was determined:

$$K_{\text{InX}} / K_{\text{In}_2\text{X}} = [\text{InX}^{3-}] [\text{In}^{3+}] / [\text{In}_2\text{X}]. \quad (9)$$

It is evident that the ratio $K_{\text{InX}} : K_{\text{In}_2\text{X}}$ must have a constant value. If the proposal

that the more positive wave described above corresponded to the reduction of indium(III) ions and the more negative wave to the reduction of In_2X chelate, the ratio $K_{\text{InX}} : K_{\text{In}_2\text{X}}$ may be calculated according to equation (9). For this calculation the values of $[\text{In}^{3+}]$ and $[\text{In}_2\text{X}]$ were read from the polarogram; concentration of InX^{3-} chelate was determined using the equation

$$C_{\text{In}} = [\text{In}^{3+}] + [\text{InX}^{3-}] + 2[\text{In}_2\text{X}], \quad (10)$$

where C_{In} is the total concentration of indium.

The value of the ratio $K_{\text{InX}} : K_{\text{In}_2\text{X}}$ was calculated according to the equation (9) for the systems containing various ratios of $C_{\text{In}} : C_{\text{X}}$ and for the pH range 3.3–4.1. From the series of measurements the average value of the ratio $K_{\text{InX}} : K_{\text{In}_2\text{X}}$ was found to be $2.8 \cdot 10^{-4}$, the maximum differences not exceeding $\pm 12\%$.

Determination of the Stability Constant of 1 : 1 Indium-TTHA Chelate

The results of the polarographic study of indium-TTHA chelates have shown that direct polarographic methods for the determination of stability constant of the chelates involved cannot be applied. Therefore the substitution equilibrium expressed by reaction (C) was studied.



The binuclear nickel-TTHA chelate was chosen because the wave of released nickel(II) ions did not interfere with the wave of indium(III) ions and that of In_2X chelate under the conditions used.

Using the polarographic technique it has been established that the product of reaction (C) are the released nickel(II) ions. During the course of reaction (C) a binuclear intermediate of the composition InNiX^- was formed; more detailed data connected with the mechanism of reaction (C) are published elsewhere¹⁰. The establishment of the equilibrium described by reaction (C) is slow. The measurements of the equilibrium concentrations were carried out approx. 60 hours after mixing of the reaction components. During the continual measurement it has been found that the wave heights of indium(III) and nickel(II) ions reached a constant value after 50 hours.

Measurement was carried out as follows: Solutions of nickel(II) sulphate and TTHA were mixed in the molar ratio 2 : 1 in the solution of perchloric acid, pH was adjusted to the desired value using the solution of sodium hydroxide and a given amount of indium(III) perchlorate was added. The resulting solution was kept for three days at the temperature approx. 40°C (at higher temperature the hydrolysis of indium salt starts). After this time period the temperature of the solution examined was adjusted to 20°C and the polarogram was recorded.

The equilibrium constant K_{III} of reaction (C) was defined by the equation

$$K_{III} = [\text{InX}^{3-}] [\text{Ni}^{2+}]^2 / [\text{Ni}_2\text{X}^{2-}] [\text{In}^{3+}] = K_{\text{InX}} / K_{\text{Ni}_2\text{X}} \quad (11)$$

In this equation the terms in brackets refer to equilibrium concentration of the species involved. The equilibrium concentration of InX^{3-} chelate was calculated using the equation

$$[\text{InX}^{3-}] = C_{\text{In}} - [\text{In}^{3+}] - 2[\text{In}_2\text{X}] \quad (12)$$

as follows according to equation (10). Similarly, the equilibrium concentration of Ni_2X^{2-} chelate was calculated using the equation defining the total concentration of nickel C_{Ni}

$$C_{\text{Ni}} = [\text{Ni}^{2+}] + [\text{NiX}^{4-}] + 2[\text{Ni}_2\text{X}^{2-}] \quad (13)$$

The term $[\text{NiX}^{4-}]$ in equation (13) was neglected because the concentration of NiX^{4-} chelate was very low due to a high difference between the stability constants of Ni_2X^{2-} and NiX^{4-} chelates ($\log K_{\text{Ni}_2\text{X}} = 29.5$; $\log K_{\text{NiX}} = 18.8$ (ref.⁹). The equilibrium concentration of nickel(II) and indium(III) ions were read directly from the polarogram.

The results of the measurement are presented in Table I which gives the values of the equilibrium constant K_{III} and the log values of the stability constant K_{InX} calculated for various initial concentrations of the reaction components of the system studied. The mean value of $\log K_{\text{InX}}$ was determined as 26.53.

TABLE I
Values of the Stability Constant of the InX^{3-} chelate Calculated According to Equation (9)
 $C_{\text{X}} = 0.5C_{\text{Ni}}$.

pH	C_{In} M. 10^4	C_{Ni} M. 10^4	$K_{III} \cdot 10^3$	$\log K_{\text{InX}}$
3.0	32.0	8.0	1.16	26.56
3.0	28.0	8.0	0.88	26.44
3.0	24.0	8.0	0.99	26.50
3.0	20.0	8.0	0.89	26.45
3.0	16.0	8.0	0.96	26.48
3.0	12.0	8.0	1.01	26.50
2.4	8.0	4.0	1.38	26.64
2.4	12.0	4.0	1.42	26.65
2.4	16.0	4.0	1.28	26.59
3.0	24.0	8.0	0.96	26.50

For the determination of the stability constant of the 1 : 1 indium-TTHA chelate, the reaction compounds at zero time must be indium(III) ions and a suitable TTHA chelate. The reverse reaction (C) reaction of InX^{3-} chelate with nickel(II) ions cannot be applied because the presence of only one type of indium-TTHA chelate cannot be supposed. Another difficulty is that the reverse reaction proceeds only when nickel(II) ions are present in a large excess against InX^{3-} chelate and this condition interferes with the possibilities of the polarographic measurement. To verify the calculated value of the stability constant K_{InX} the 2 : 1 nickel-TTHA chelate in reaction (C) was replaced by 2 : 1 zinc-TTHA chelate. Stability constant of Zn_2X^{2-} chelate has the value close to $K_{\text{Ni}_2\text{X}}$ ($\log K_{\text{Zn}_2\text{X}} = 28.7$) (ref.¹¹) and released zinc(II) ions may be easily determined polarographically in the presence of indium(III) ions. It has been, however, found that during the reaction of Zn_2X^{2-} chelate with indium(III) ions, practically all zinc(II) ions were released and the calculation of the corresponding equilibrium constant was not accurate.

Determination of the Stability Constant of Binuclear Indium-TTHA Chelate

The stability constant of the 2 : 1 indium-TTHA chelate was calculated from the previously determined value $K_{\text{InX}} : K_{\text{In}_2\text{X}}$ and from the value K_{InX} . Using these relations the stability constant of binuclear indium-TTHA chelate was calculated; the value $\log K_{\text{In}_2\text{X}}$ was found to be 30.11.

Calculation of Equilibrium Concentration of In_2X Chelate

Equilibrium concentration of InX^{3-} or In_2X chelate in the solution containing indium(III) ions and the reagent can be calculated when the corresponding stability constants and total concentrations are known. In the case studied the attempt to express the concentration of In_2X chelate as the function of total reagent and total indium concentration and the corresponding stability constant led to the equation of higher order. The concentration of In_2X chelate was therefore expressed as the function of the stability constant $K_{\text{In}_2\text{X}}$, concentration of indium(III) ions $[\text{In}^{3+}]$ and total reagent concentration C_X . Calculated concentration of In_2X chelate was compared with the In_2X chelate concentration determined by the measurement of the more negative wave as described above.

Total concentration of the reagent C_X was defined by the expression

$$C_X = [\text{InX}^{3-}] + [\text{In}_2\text{X}] + [\text{X}^{6-}] + [\text{H}_n\text{X}^{6-n}], \quad (14)$$

where n has the value 1–6. According to equations (5) and (7) the concentration of InX^{3-} and In_2X chelates was expressed by the equations

$$[\text{InX}^{3-}] = K_{\text{InX}}[\text{In}^{3+}][\text{X}^{6-}], \quad (15)$$

$$[\text{In}_2\text{X}] = K_{\text{In}_2\text{X}}[\text{In}^{3+}]^2 [\text{X}^{6-}]. \quad (16)$$

When the concentration of the protonized forms of TTHA was expressed with the use of the dissociation constants K_1, K_2, K_3, K_4, K_5 and K_6 and with the use of equations (15) and (16), the equation (14) was transformed as

$$C_X = ([\text{X}^{6-}] [\text{H}^+]^6 / K_1 K_2 K_3 K_4 K_5 K_6) + K_{\text{InX}}[\text{In}^{3+}] [\text{X}^{6-}] + K_{\text{In}_2\text{X}}[\text{In}^{3+}]^2 [\text{X}^{6-}]. \quad (17)$$

From equation (17) it follows that

$$[\text{X}^{6-}] = \frac{C_X}{K_{\text{InX}}[\text{In}^{3+}] + K_{\text{In}_2\text{X}}[\text{In}^{3+}]^2 + ([\text{H}^+]^6 / K_1 K_2 K_3 K_4 K_5 K_6)}, \quad (18)$$

Because $[\text{H}^+]^6 / K_1 K_2 K_3 K_4 K_5 K_6 \ll K_{\text{InX}}[\text{In}^{3+}]$, the value of this term was neglected and by combination of equation (18) with equations (15) and (16), the concentration of In_2X chelate was formulated as

$$[\text{In}_2\text{X}] = K_{\text{In}_2\text{X}} C_X [\text{In}^{3+}] / (K_{\text{InX}} + K_{\text{In}_2\text{X}}[\text{In}^{3+}]). \quad (19)$$

According to equation (19), concentration of In_2X chelate was calculated using the known values of C_X , K_{InX} and $K_{\text{In}_2\text{X}}$ and from polarographically determined concentration of indium(III) ions. The results are presented in Table II, together with the values of $[\text{In}_2\text{X}]$ determined experimentally by the measurement of the second (more negative) wave, obtained in the system containing TTHA reagent and an excess of indium(III) ions. Satisfactory agreement of experimental and theoretical data in Table II verify the validity of the proposal presented in this study.

TABLE II

Calculated and Experimentally Determined Values of In_2X Chelate Concentration pH 4.8; measured 24 hours after mixing.

C_X M. 10^4	C_{In} M. 10^4	[In_2X], M. 10^4	
		calculated	experimental
4.0	5.6	0.90	0.85
4.0	6.4	1.09	1.10
4.0	7.2	1.74	1.35
4.0	8.0	1.95	1.76
2.0	5.0	1.10	0.96
2.0	6.0	1.21	1.15

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