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A Method for Studying Mixed Hydroxo Complexes within the *p*H Range where the Ligand is not Protonated

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A general method is presented, which can be used for the determination of the composition (j, p) of soluble mononuclear mixed hydroxo complexes, $[B(OH)_jA_p]$, formed in the presence of an excess of the ligand and within the *p*H range in which the ligand is not protonated. In order to find the value of j two titration curves are compared: (1) the curve obtained when a solution of pure alkali or ammonium salt of a polybasic acid, $A = \text{const.}$, is titrated with strong acid of total concentration a_s; (2) the curve obtained when the same solution as above is titrated with addition of a small amount of metal ions, $B = \text{const.}$, the condition being $B \ll A$. The difference (Δ) of *p*H between the two curves at $a_s = 0$ is explained, exclusively as being an effect of the metal ions. There are three possible cases that should be taken into consideration:

1. $\Delta = 0$; The mixed hydroxo complexes are either not formed, or the initially hydrolyzed composite central group $[B(OH)_2]$ is not further hydrolyzed; Bjerrum's method[6] can be applied to find the p value. A thorium oxalate complex[4] is given as an example.

2. $\Delta > 0$; OH ions from the initially hydrolysed composite central group, $[B(OH)_2]$ are replaced by the ligand. A zirconyl oxalato complex[11] is given as an example.

3. $\Delta < 0$; Mixed hydroxo complexes are formed. Thorium maleato[3] and thorium phthalato[2] complexes are given as examples.

In the cases 2. and 3., where Bjerrum's method can not be applied, the solubility curve of metal hydroxide in an excess of ligand, can be used to find the p value.

INTRODUCTION

Precipitation studies of the thorium ion in the presence of phthalate[1,2], maleate[3] and oxalate[4] have shown that soluble complexes are formed at relatively high *p*H values and in presence of an excess of ligand. Because of the formation of the precipitate at low *p*H values[1-4], where the ligand is combined with a proton, Bjerrum's method[6] of competitive reactions is hardly applicable. Also before any calculation of equilibrium constants is attempted one should test the system for the possible presence of soluble mixed hydroxo complexes[5]. Österberg's graphical method[7] can be successfully applied in most studies of mixed hydroxo complexes when the ligand is not present in considerable excess over the metal ion, and at *p*H values at which it is protonated.

In this work a simple method is described for studying soluble mixed hydroxo complexes in the presence of a large excess of ligand, within the *p*H range where the ligand is not protonated. These very frequently observed conditions are usually regarded as inconvenient for studying the formation of complexes and are often avoided.

THE GENERAL METHOD

Two following titration curves representing -log [H$^+$] as a function of a_s, are compared: 1. The titration curve of the alkali or ammonium salt of a polybasic acid, titrated with strong acid (concentration A = const.). The total concentration, a_s, of the strong acid is calculated for each titration point. 2. The titration curve of the alkali or ammonium salt of a polybasic acid titrated with strong acid (A = const.) with a small amount of metal ion, B = const., being added to the salt solution. The condition is $B \ll A$.

The titration curve 2 should be experimentally determined, whereas curve 1 can be either experimentally determined or calculated from acidity constants if they are accurately known. According to literature[8], the estimating of the titration curves is based on estimating of the *p*H values for each titration point using approximative methods. The full equation may be of high degree, depending on the number of ionization constans. The polynomial expression for h (where h is the free hydrogen ion concentration), for the alkali salt of a dibasic acid titrated with strong acid is

$$h^4 + h^3 (2A - a_s + K_1) + h^2 [K_1K_2 + K_1 (A - a_s) - K_W] - \\ - h \cdot K_1 [K_2a_s + K_W] - K_1K_2K_W = O \qquad (1)$$

A trial and error method is usually used to evaluate particular parts of the titration curve[8]. However, the establishing of theoretical titration curves can be much simpler if a value for h is assumed and a_s is evaluated. According to N. Bjerrum[9], if the stoichiometric over-all stability constants, β_j, of the polybasic acid, H_jA, are known, it is possible to evaluate Z(h):

$$Z(h) = \frac{\sum_{1}^{J} j \cdot \beta_j \cdot h^j}{\sum_{0}^{J} \beta_j \cdot h^j} \qquad (2)$$

where J stands for the maximum value of j and represents the basicity of the polybasic acid. Z is the average number of ligands bound to one central group A. From experimental data the value of Z(h) is

$$Z(h) = \frac{a_s - h + K_W/h}{A} \qquad (3)$$

Calculated Z curves, Z(h) *vs.* -log [H$^+$], can be used as »calibration curves«. For any assumed value h, the value of Z (h) is taken from the calibration curve and a_s is estimated

$$a_s = Z(h) \cdot A + h - K_W/h \qquad (4)$$

Thus from the assumed values of h and evaluated values of a_s it is possible to establish the titration curve in its usual form (-log [H$^+$] *vs.* a_s) and to compare it with the one obtained in presence of the metal ion.

It can be assumed that when $a_s = 0$, the ligand is not combined with the H^+ ion. When the ligand is in large excess with respect to the metal ions, the amount of ligands bound to the metal can be neglected. Any difference (Δ) in -log $[H^+]$ between the two curves compared at $a_s = 0$ is due to the added metal ions. Three possible effects of the metal ions will be discussed.

1. A small amount of metal ions added to the solution does not change the values of -log $[H^+]$ at $a_s = 0$, *i. e.* $\Delta = 0$. The general equations for mononuclear complex formation are:

a) in the case of the simple ion:

$$B + pA = BA_p \tag{5}$$

b) in the case of the composite ion:

$$BO + H_2O = B(OH)_2 \tag{6}$$

$$B(OH)_2 + pA = B(OH)_2A_p \tag{7}$$

This is the simplest case, and Bjerrum's[6] method can be used for the calculation of the p value.

2. A small amount of metal ions added to the solution increases the value of -log $[H^+]$ at $a_s = 0$, *i. e.* $\Delta > 0$ in the case when the substitution takes place and OH^- is released from the initially hydrolyzed composite central group, $[B(OH)_2]$. The general equations for complex formation are eqs. (6—8)

$$B(OH)_2A_p + A = BA_{p+1} + 2OH \tag{8}$$

From the difference between the two titration curves, $\Delta\, a_s$, in the range of -log $[H^+]$ values in which the ligand is not protonated, it is possible to estimate the amount of the formed $B\,A_{p+1}$ complex by using equation

$$[BA_{p+1}] = \Delta\, a_s/2 \tag{9}$$

Assuming that all metal ions are in the complex form, it is possible to estimate the amount of $B(OH)_2A_p$ complex using the equation

$$[B(OH)_2A_p] = B - \Delta\, a_s/2 \tag{10}$$

The concentration of the free ligand, a, is approximately

$$a = A - (p + 1)\,B \tag{11}$$

From experimental data, using eqs (9)—(11), it is possible to estimate the equilibrium constant of the reaction represented by eq. (8). In the estimating of the p value, it should be taken into consideration that complexes with two different central groups exist (B and $B(OH)_2$).

3. A small amount of metal ions added to the solution decreases the value of -log $[H^+]$ at $a_s = 0$, *i. e.* $\Delta < 0$, indicating that hydrolyzed complexes are formed. The general equations are:

a) for simple metal ions:

$$B + jH_2O + pA = B(OH)_jA_p + jH^+ \tag{12}$$

b) for composite metal ion eq. (6) and

$$B(OH)_2 + jH_2O + pA = B(OH)_{2+j}A_p + jH^+ \tag{13}$$

From the difference between the two titration curves, Δa_s, at -log [H^+] values where the ligand is not protonated, it is possible to estimate the j value:

$$j = \Delta a_s/B \tag{14}$$

Once the j value is found, the direct solubility method[5] can be applied to the study of mixed complexes which are mononuclear with respect to the metal ion. From the precipitation boundary between solid metal hydroxide and the soluble mixed hydroxo complex obtained by the tyndallometric method, the p value can be found. For various B values, the corresponding pairs of -log [H^+] and A values at which metal hydroxide starts to precipitate should be found experimentally. In the presence of a large excess of ligand and at high -log [H^+] values, it can be assumed that

$$[B(OH)_jA_p] \approx B \tag{15}$$

$$a = A - pB \tag{16}$$

The general reaction of the dissolution of metal hydroxide in an excess of ligand is

$$B(OH)_v(s) + (v - j)\, H^+ + pA = B(OH)_jA_p + (v - j)\, H_2O \tag{17}$$

where v denotes the valency of the metal ion.

The dissolution constant for the reaction represented by the eq. (17) is

$$K_0 = \frac{[B(OH)_jA_p]}{h^{v-j}a^p} \tag{18}$$

Eqs. (14) and (15) are introduced into eq. (18). The logarithmic form of the obtained equation is

$$\log K_0 = \log \frac{B}{(A - pB)^p} - (v - j) \log [H^+] \tag{19}$$

Assuming different low integer values for p, the value of log K_0 can be estimated from the experimental data using eq. (19). An approximately constant value of log K_0, seems to be a proper criterion for the determination of the p value. If the solubility product of the metal hydroxide, $K_{SO} = b\,[OH]^v$, can be determined independently, and if K_0 was determined at the constant ionic strength, it is possible to calculate the accurate formation constant β_{jp} for the reaction (12) by using eq. (20):

$$\beta_{jp} = K_0 K_W{}^{v-j}/K_{SO} \tag{20}$$

where

$$\beta_{jp} = \frac{[B(OH)_jA_p]}{b[OH]^ja^p} \tag{21}$$

and b is the free metal ion concentration.

APPLICATION TO EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1 are represented calculated parts of Z curves, which were used as calibration curves: curve 1, maleic acid at 20 °C, μ var. The value $\beta_1 = 10^6$ was previously determined; curve 2, phthalic acid at 20 °C, μ var. The value $\beta_1 = 8.9 \cdot 10^4$ was previously determined; curve 3, oxalic acid at 20° C, μ var. The literature values $\beta_1 = 1.15 \cdot 10^4$ and $\beta_2 = 1.82 \cdot 10^5$ were used for calculations[10]. Using the calibration curve 3 (Fig. 1) and eq. (4), it is possible to estimate titration curves for various concentrations of the oxalate ion. Such calculated curves are shown in Fig. 2. together with some experimental points, which were used to check the validity of such estimatings.

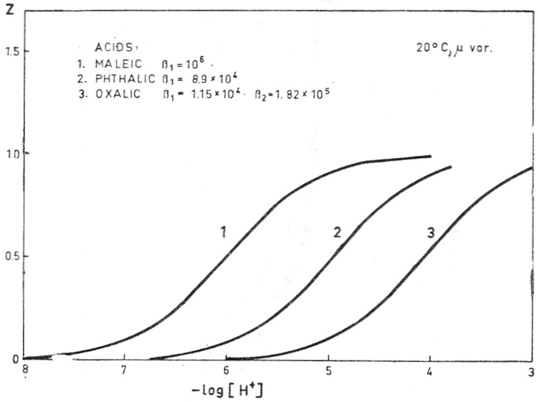

Fig. 1. Z curves calculated, using eq. (27) are plotted in the graph (Z(h) *vs.* — log [H^+], for the following organic acids: 1, maleic acid, at 20° C, μ var. The value $\beta_1 = 1.0 \times 10^6$ was previously determined; 2, phthalic acid, at 20° C, μ var. The value $\beta_1 = 8.9 \times 10^4$ was previously determined; 3, oxalic acid, at 20° C, μ var. Literature values[10] $\beta_1 = 1.15 \times 10^4$ and $\beta_2 = 1.82 \times 10^5$ were used.

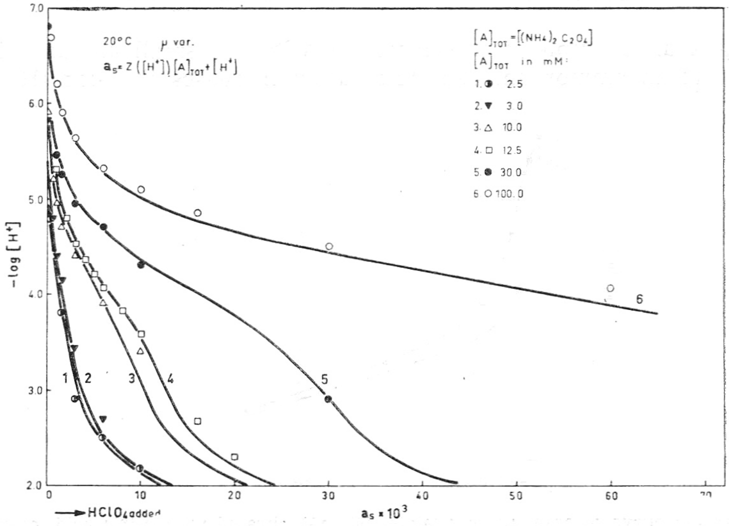

Fig. 2. Titration curves of ammonium oxalate of const. concentration, A, titrated with strong acid, were calculated using eq. (4) and (2) and represented in the diagram — log [H^+] *vs.* a_s: 1. 2.5 m*M*; 2. 3.0 m*M*; 3. 10.0 m*M*; 4. 12.5 m*M*; 5. 30.0 m*M*; 6. 100.0 m*M*; Several experimental points were used to verify the validity of this calculation; 20° C, μ var.

The experiments were performed as described in earlier works[2-4] and seem to agree with the calculated curves.

In Fig. 3 an example is shown where $\Delta = 0$. The addition of thorium ion to ammonium oxalate solution does not change -log $[H^+]$ at $a_s = 0$, consequently, no mixed hydroxo complexes are formed. The value $p = 4$ was found earlier[4] by applying Bjerrum's method[6].

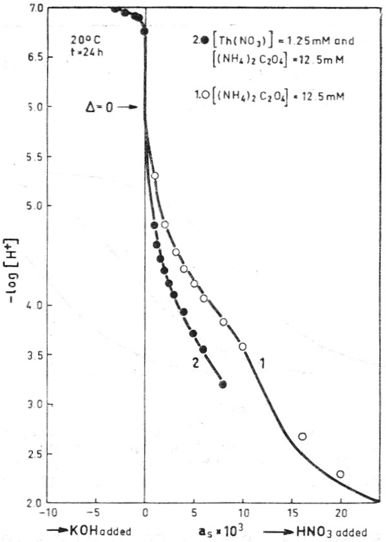

Fig. 3. 1, titration curve of ammonium oxalate, 12.5 m*M*, titrated with nitric acid, calculated from eq. (4) using »calibration curve« 3 (Fig. 1). Experimental points are indicated by circles. 2, titration curve of 12.5 m*M* ammonium oxalate and 1.25 m*M* $Th(NO_3)_4$, titrated with nitric acid and potassium hydroxide, obtained experimentally and indicated by dots. The difference (Δ) in $-\log [H^+]$ between titration curves 1 and 2 at $a_s = 0$ is zero.

In Fig. 4 an example is shown where $\Delta > 0$. A small amount of zirconyl ions added to an ammonium oxalate solution increases the -log $[H^+]$ value at

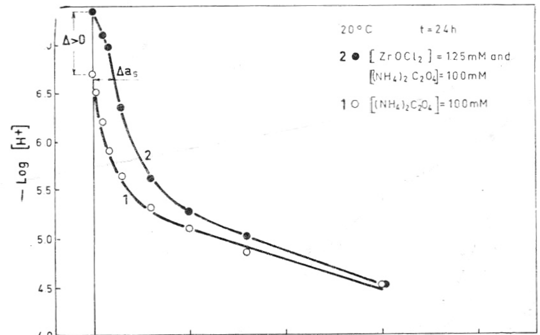

Fig. 4. 1, titration curve of ammonium oxalate, 100 m*M*, titrated with nitric acid, calculated from eq. (4), using »calibration curve« 3 (Fig. 1). Experimental points are indicated by circles. 2, titration curve of 100 m*M* ammonium oxalate and 1.25 m*M* $ZrOCl_2$, titrated with nitric acid and potassium hydroxide, obtained experimentally and denoted by dots. The difference (Δ) in $-\log [H^+]$, between titration curves 1 and 2 at $a_s = 0$ is $\Delta > 0$[11].

$a_s = 0$. This suggests that the OH ions from the hydrolyzed composite ion, ZrO^{2+}, are replaced by the oxalate ion. The value $p = 3$ was estimated using eq. (19), in the concentration range in which equal electrophoretic mobilities were observed[11].

In Fig. 5 an example is shown where $\Delta < 0$. Calibration curve 1 (Fig. 1) and eq. (4) are used to calculate curve 2 (Fig. 5). Experimental points are indicated by circles. A small amount of thorium ions added to a potassium maleate solution decreases the -log $[H^+]$ value at $a_s = 0$, indicating that mixed hydroxo complexes are formed. The value for p has not yet been determined[3].

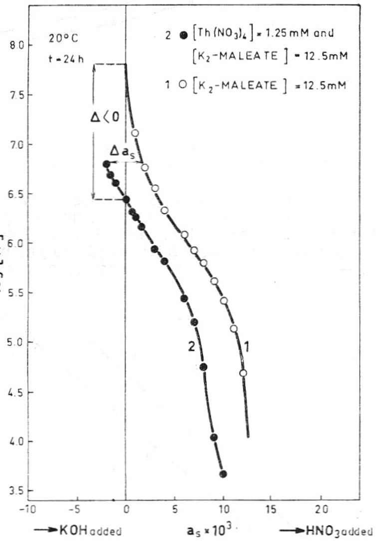

Fig. 5. 1, titration curve of potassium maleate, 12.5 m*M*, titrated with nitric acid, calculated from eq. (4), using »calibration curve« 1 (Fig. 1). Experimental points are indicated by circles. 2, titration curve of 12.5 m*M* potassium maleate and 1.25 m*M* $Th(NO_3)_4$ titrated with nitric acid and potassium hydroxide, obtained experimentally and denoted by dots. The difference (Δ) in $-\log[H^+]$, between titration curves 1 and 2 at $a_s = 0$ is $\Delta < 0$.

Another example, where $\Delta < 0$ is shown in Fig. 6. A small amount of thorium ions added to a potassium phthalate solution decreases the value -log $[H^+]$ at $A_s = 0$[2]. Using eq. (13), the value $j = 2$ was found by comparing a number of titration curves. The soluble complex $Th(OH)_2(Phth.)_p$ is in equilibrium with solid thorium hydroxide and eqs. (14)—(20) can be applied to find the p value and to estimate the formation constant, β_{jp}, defined by eq. (21).

Fig. 7 shows the solubility boundary between thorium hydroxide and the soluble thorium hydroxo phthalate complex at $pH = 7.6$ and $pH = 7.4$, respectively, obtained by tyndallometric measurements. Data[2] obtained earlier were extended and are represented in the plot of log $[Th]_{tot}$ *vs.* log $[Phth.]_{tot}$. By inserting these data and the assumed p values ($p = 0, 1, 2, 3$) into eq. (19) it was possible to estimate log K_0 for each p value, as shown in Fig. 8.

For $p = 1$ an approximately constant value log $K_0 = 12.75$ is obtained. Therefore one can assume that in the presence of a large excess of the phthalate ions and at high *p*H, the neutral complex $[Th(OH)_2Phth^0]$ is formed. It was found earlier[1] that neutral electrolytes containing Li^+, Na^+, K^+, Ca^{2+},

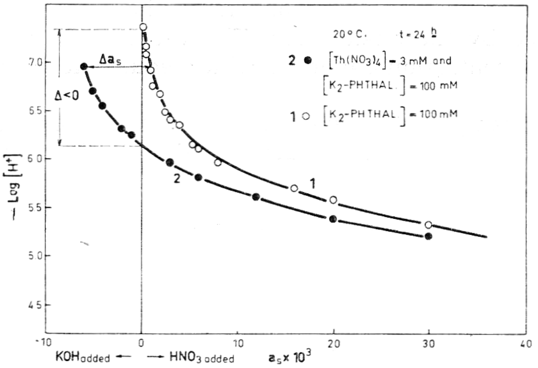

Fig. 6. 1, titration curve of 100 m*M* potassium phthalate titrated with nitric acid, calculated from eq. (4), using »calibration curve« 2 (Fig. 1). Experimental points are indicated by circles. 2, titration curve of 100 m*M* potassium phthalate and 3 m*M* $Th(NO_3)_4$ titrated with nitric acid and potassium hydroxide, obtained experimentally and experimental points are denoted by dots. The difference (Δ) in — log [H^+], between titration curves 1 and 2 at $a_s = 0$ is $\Delta < 0$.

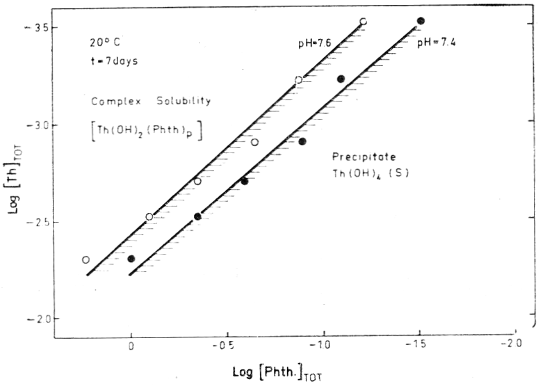

Fig. 7. Solubility boundary between thorium hydroxide and the soluble thorium hydroxo phthalate complex, at *p*H = 7.6 and *p*H = 7.4, obtained by tyndallometric technique and represented in the graph log $[Th]_{tot}$ *vs.* log $[Phth.]_{tot}$. Earlier data[2] were extended.

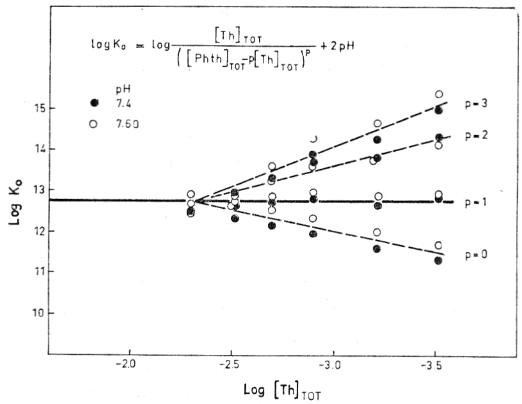

Fig. 8. The value of log K_0, where K_0 is defined by eq. (18) is calculated according to eq. (19) and plotted *vs.* log $[Th]_{tot}$, the value of p in the complex $[Th(OH)_2Phth_p]$ being the parameter.

Mg^{2+}, La^{3+}, and Y^{3+} significantly affected the precipitation when added to soluble thorium phthalato complexes in the region which is limited toward lower *p*H values by solid thorium hydroxo phthalate. From the change of *p*H and from high coagulation values it could be concluded that the coagulation is not the only phenomenon to be considered. Probably the addition of the mentioned cations causes the formation of a new solid phase, containing the complex anion. The composition of the formed solid phase in the presence of neutral electrolytes has not yet been determined. However, when neutral electrolytes were added in high concentrations to soluble complexes in the region which is limited with solid $Th(Phth.)_2$, *i. e.* in the presence of a large excess of phthalate, no solid phase was observed[1]. This might be the proof of the presence of the neutral complex $[Th(OH)_2Phth^0]$ in this region as it was concluded from Fig. 8. Earlier values for the solubility product of thorium hydroxide, $\log K_{SO} = -45.68$[12], $\log K_{W,\, 20^0C} = 14.16$[10] and the calculated value $\log K_0 = 12.75$ were introduced into eq. (20). The approximate value for the formation constant, $\log \beta_{21} = 30$, was obtained (the ionic strength was not constant).

As far as the author knows, in the literature there are no other equilibrium data on the soluble thorium hydroxo phthtalato complexes available for comparison.

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IZVOD

Metoda određivanja miješanih hidrokso kompleksa u *p*H području gdje ligand nije protoniziran

H. Bilinski

Prikazana je opća metoda za određivanje p i j vrijednosti topljivog mononuklearnog miješanog hidrokso kompleksa $[B(OH)_jA_p]$, koji nastaje u suvišku liganda i u *p*H području, gdje ligand nije protoniziran. Za određivanje j vrijednosti uspoređene su: 1. krivulja titracije alkalijske ili amonijeve soli polibazne kiseline (A = konst.), s jakom kiselinom totalne koncentracije a_s i 2. krivulja titracije analogne koncentracije soli uz mali dodatak metalnog iona (B = konst.), s jakom kiselinom

koncentracije a_s. Uvjet je $B \ll A$. Ukoliko postoji neka razlika Δ u $-\log [H^+]$ između dviju uspoređenih krivulja kod $a_s = 0$, onda se ona isključivo može pripisati efektu metalnog iona. Opisana su tri moguća slučaja:

$\Delta = 0$; miješani hidrokso kompleksi ili ne nastaju, ili početno hidrolizirana složena centralna grupa (BO) dalje ne hidrolizira. Bjerrumova metoda[6] može se upotrijebiti za određivanje p vrijednosti. Torijev oksalato kompleks[4] prikazan je kao primjer.

2. $\Delta > 0$; ligand zamjenjuje OH ione iz početno hidrolizirane složene centralne grupe. Cirkonil oksalato kompleks[11] pokazan je kao primjer.

3. $\Delta < 0$; nastaju miješani hidrokso kompleksi. Kao primjer pokazani su torijev maleato-[3] i torijev ftalato[2]-kompleks.

U slučaju 2. i 3., gdje se Bjerrumova metoda[6] ne može primijeniti, za određivanje p vrijednosti može se upotrijebiti krivulja topljivosti metalnog hidroksida u suvišku liganda.

Opisana metoda može se upotrijebiti prije tačnih računanja ravnotežnih konstanata.

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ZAGREB

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