Journal of the University of Chemical Technology and Metallurgy, 41, 2, 2006, 211-216

EFFECT OF FORMATION CONSTANT OF SOME METALS ON THE ENHANCEMENT OF THE ACIDITY OF A WEAK ACID H_2Y^{2-} (DISODIUM ETHYLENEDIAMINETETRACETIC ACID)

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Received 24 March 2006
Accepted 30 May 2006

ABSTRACT

The dissociation constants of H_2Y^{2-} *and the formation constants of its complexes with different metals ions were evaluated by potentiometric measurements in aqueous solution. This study shows that the presence of metallic ion whose pKc values is less than 10.0 like Ba(II), Mg(II) and Ag(I) causes an increase of the last acidity of* H_2Y^{2-} (HY^{3-}/Y^{4-})*. While the other ions whose pKc are greater than 10.0 like Co (II), Ni (II) and Ca (II) cause an increase of the two acidities* (H_2Y^{2-}/HY^{3-}) *and* (HY^{3-}/Y^{4-})*.*

Keywords: enhancement of the acidity, potentiometry, formation constants, acidity constants, EDTA.

INTRODUCTION

It is known that the complexation of weak acid HL with a metallic ion or other reagents increases the acidity of the weak acid. The weak boric acid (HBO_2) with a pKa of 9.25 becomes stronger in the presence of mannitol or glycerol [1, 2]. The increase of acidity was found dependent on the concentration of glycerol [2]. The pKa value (9.8) for the last acidity of nitrilotriacetic acid becomes 6.0 in presence of Ba (II) ion due to complexation [1]. Also the pKa of NH_4^+ decreases from 9.2 to 5.1 when methanal (CH_2O) was added because of formation of $(CH_2)_6N_4H^+$ complex [3]. Similar observation was obtained with HPO_4^{2-} in presence of Ag (I) [3].

Recently, the titration curves of Ampicillin in presence of different metallic ions show that the titration metal curves are lowered compared to free Ampicillin curve. The greater deviation indicates higher complex stability. Also the change in the shape of titration curves indicates that the behavior of H^+ liberation from Ampicillin differs between Fe (III) and Cd (II) [4, 5]. The authors related this to the average radii of the metal ions in the complexes.

In order to elaborate this point, we have chosen an important complexing agent H_2Y^{2-} (disodium ethylenediaminetetracetic acid). The pK_{ai} values of H_4Y are in the order 2.0, 2.7, 6.2, and 10.2 [1]. The last acidity is very weak and expected to increase by complexation. We have chosen for this purpose two groups of metallic ions, the first one whose pKc with EDTA is less than 10.0 such as Ag (I), Ba (II) and Mg (II). The second one has pKc greater than 10.0 such as Ca (II), Ni (II) and Co (II) [1]. Also we have calculated the formation constants of complex ML for various metals with H_2Y^{2-} according to previously published method [6]. The increase in acidity was related to the strength of complexation.

EXPERIMENTAL

The potentiometric measurements were carried out using Toledo 220 M pH-meter fitted with Toledo combined glass electrode (reading ± 0.01 pH unit). The pH meter was calibrated from time to time using two standard buffer solutions 4.0 and 7.0. All of the reagents used were purchased from BDH products. All solutions were prepared in deionized water. Sodium hydroxide solution (0.10 M) was standardized against 0.10 M oxalic acid. Metallic ions solutions were standardized with EDTA solution [7].

Potentiometric procedure

The acid dissociation constant of H_2Y^{2-} were determined at 20°C by introducing 10 ml of H_2Y^{2-} (0.10 M) into a beaker of 150 ml and diluted to 40.0 ml with deionized water, then titrated with NaOH (0.10 M).

The acid-base titration technique was used in order to compute the formation constants of the complexes. The solution in the titration beaker consisted of 5.0 to 25.0 ml of metallic ions solutions (0.05 M), 10.0 ml H_2Y^{2-} solution (0.10 M) and diluted to 40 ml with deionized water. The pH readings were taken after each addition of 0.2 or 0.1 ml of NaOH solution (0.10 M).

THEORY

Calculation of $\bar{n}_H$ and pK_{ai} of the Ligand H_2Y^{2-}

We have applied Bjerrum's method [6] to calculate $\bar{n}_H$ the average number of protons associated with the ligand H_2Y^{2-} and pK_{ai}, where K_{ai} is the acid dissociation constant

$$n_H = \frac{\sum_0^n n[H_nL]}{\sum_0^n [H_nL]} = \frac{\sum_0^n nK_n^H[H]^n}{\sum_0^n K_n^H[H]^n} \qquad (1)$$

K_n^H : global acidity formation $(K_2^H = K_{a1}^H K_{a2}^H)$ and $K_{ai}^H = 1/K_{ai}$

The H_2Y^{2-} has theoretically two acid functions:

$$n_H = \frac{(2[H_2Y^{2-}]+[HY^{3-}])}{([H_2Y^{2-}]+[HY^{3-}]+[Y^{4-}])} \qquad (2)$$

$$\frac{2K_2^H[H^+]^2 + K_1^H[H^+]}{K_2^H[H^+]^2 + K_1^H[H^+] + 1} = f([H^+]) \qquad (3)$$

n_H is calculated experimentally from the titration curve

$$n_H = \frac{2[H_2Y^{2-}]_0 - [Base] - [H^+] + [OH^-]}{[H_2Y^{2-}]_0} \qquad (4)$$

Base is the concentration of NaOH in solution. $[H_2Y^{2-}]_0$ represent the analytical concentration, $[H_2Y^{2-}]_0 = f.[H_2Y^{2-}]$ (f is the dilution factor). The plot of pH against n_H gave pK_{a1} and pK_{a2} values at $n_H = 0.5$ and 1.5, respectively.

Calculation of pKc and $\bar{n}$

$\bar{n}$ is the average number of moles of ligand bound per mole of metal ion were calculated also by Bjerrum's method:

$$\bar{n} = \frac{[complex]}{[M(II)]_0} = \frac{[MY^{2-}]}{[M(II)]+[MY^{2-}]} \qquad (5)$$

Replacing $[MY^{2-}]$ by $\beta[MY^{2-}][Y^{4-}]$ we obtained:

$$\frac{\beta[M(II)][Y^{4-}]}{[M(II)]+\beta[M(II)][Y^{4-}]} = \frac{\beta[Y^{4-}]}{1+\beta[Y^{4-}]} \qquad (6)$$

β being 1/Kc, where Kc is the complex dissociation constant. $\bar{n}$ can be calculated from the titration curve and the formation constants of acidity $K_{a1}^H(HY^{3-}/Y^{4-})$ and $K_{a2}^H(H_2Y^{2-}/HY^{3-})$.

$$K_{a2}^H = \frac{[H_2Y^{2-}]}{[H^+].[HY^{3-}]} \text{ and } K_{a1}^H = \frac{[HY^{3-}]}{[H^+].[Y^{4-}]} \qquad (7)$$

$$\bar{n} = \frac{\left([H_2Y^{2-}]_0 - [H_2Y^{2-}] - [HY^{3-}] - [Y^{4-}]\right)}{[M(II)]_0} =$$

$$= \frac{\left[H_2Y^{2-}\right]_0 - K_{a1}^H K_{a2}^H \left[H^+\right]^2 \left[Y^{4-}\right] - K_{a1}^H \left[H^+\right]\left[Y^{4-}\right] - \left[Y^{4-}\right]}{[M(II)]_0} =$$

$$= \frac{\left[H_2Y^{2-}\right]_0 - \left[Y^{4-}\right](K_{a1}^H K_{a2}^H \left[H^+\right]^2 + K_{a1}^H \left[H^+\right] + 1)}{[M(II)]_0} \qquad (8)$$

[M (II)]$_o$ and [H$_2$Y^{2-}]$_o$ represent the analytical concentrations.

[Y^{4-}] is obtained as follows:

$$2[H_2Y^{2-}] + [HY^{3-}] = 2[H_2Y^{2-}]_0 - [Base] - [H^+] + [OH^-]$$

$$= \left[Y^{4-}\right].\left(2K_{a1}^H K_{a2}^H \left[H^+\right]^2 + K_{a1}^H \left[H^+\right]\right)$$

$$[H^+] = 10^{-pH} \quad \text{and} \quad [OH^-] = 10^{-14}/[H^+]$$

$$\left[Y^{4-}\right] = \frac{2\left[H_2Y^{2-}\right]_0 - [Base] - \left[H^+\right] + \left[OH^-\right]}{2K_{a1}^H K_{a2}^H \left[H^+\right]^2 + K_{a1}^H \left[H^+\right]} \qquad (9)$$

For each couple (pH, B) we calculate $\bar{n}$ and [Y^{4-}] then by plotting n values versus p[Y^{4-}] the pK$_c$ values are obtained at p [Y^{4-}] equivalent to $\bar{n}$ = 0.5, 1.5, ... and $\bar{n}$ corresponds to the limit of n in the curve $\bar{n} = f(p\left[Y^{4-}\right])$.

RESULTS AND DISCUSSION

Acidity constant studies: Titration of H$_2$Y^{2-}

10.0 ml of H$_2$Y^{2-} (0.10 M) was titrated with NaOH (0.10 M). The titration curve shows only one jump at volume equal 10.0 ml. Fig. 1. The pH at V (NaOH) = 0.0, 5.0 and 10.0 ml are 4.40, 6.20 and 8.00, respectively. The experimental pH 4.40 corresponds to a theoretical value of an amphoteric solution made up mainly of H$_2$Y^{2-}. The pH of this solution $= (pK_{a3} + pK_{a2})/2 = (2.7 + 6.2)/2 = 4.45$. Similarly pH 8.00 corresponds to HY^{3-} amphoteric solution, and it is equal to $= (pK_{a2} + pK_{a1})/2 = (6.2 + 9.8)/2 = 8.0$

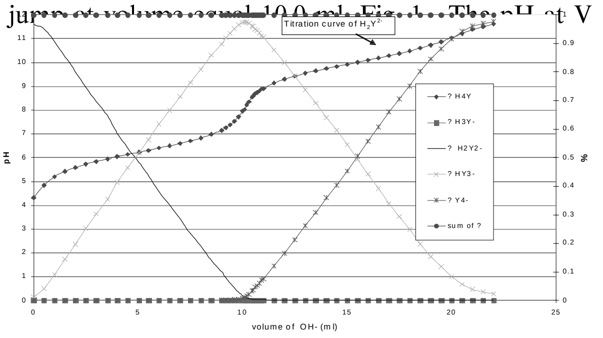

Fig. 1. Titration curve of 10.0 ml H$_2$Y^{2-} (0.10 M) with NaOH (0.10 M).

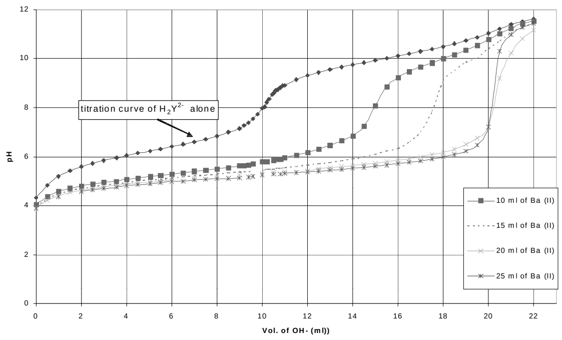

Fig. 2. Titration curves of 10.0 ml of H$_2$Y^{2-} (0.10 M) in presence of x ml of Ba (II) (0.05 M) with NaOH (0.10 M) (x = 10.0, 15.0, 20.0, 25.0 ml).

The % of EDTA species are calculated at each volume of NaOH added. The corresponding curves are shown in Fig. 1. These curves show that % H$_2$Y^{2-} (at V = 0) is 96 % the remaining are 2 % for HY^{3-} and 2 % for H$_3$Y$^-$ according to the reaction:

$$2H_2Y^{2-} \rightleftharpoons HY^{3-} + H_3Y^-$$

The % curves for HY^{3-} and for Y^{4-} are not linear after V = 18.5 ml. They intersect at 15.5 ml of NaOH instead of 15.0 ml. The latter corresponds to the second half equivalence point. This means that the neutralization of HY^{3-} is not quantitative at 100 %. Also the % HY^{3-} left is about 9 % after addition of 20 ml of NaOH. This confirms the weakness of the acidity of HY^{3-}. This acidity however can be reinforced by complexation with a metallic ion. The plots of $\bar{n}_H$ vs pH curve indicates that $\bar{n}_H$ increases to 2.0. The values of pK$_{a1}$ and pK$_{a2}$ are taken equal to pH values 9.8 and 6.2 corresponding to $\bar{n}_H$ = 0.5 and 1.5 respectively. The pK$_{ai}$ values are very close to published values [1] and will be used to calculate the dissociation constant pKc MY^{2-}.

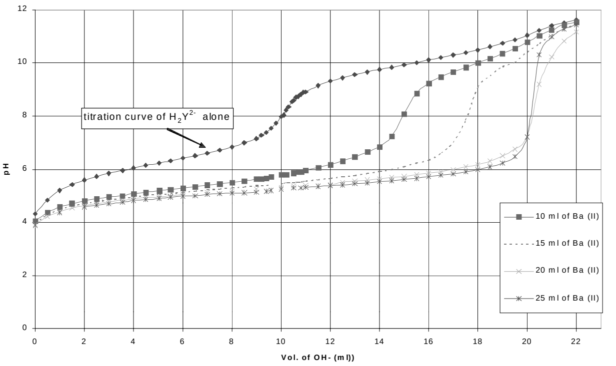

Fig. 3. Variation of the percentages of important species versus ml OH^- during titration of 10.0 ml of H_2Y^{2-} (0.10 M) and 10.0 ml of Ba (II), 0.05 M with NaOH (0.10 M).

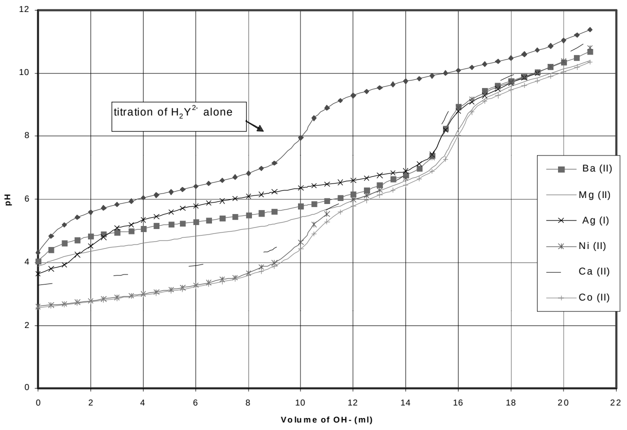

Fig. 4. Comparison of different titration curves of 10.0 ml of H_2Y^{2-}(0.10 M) in presence of 10.0 ml of different metallic ion (0.05 M).

Complex formation studies

Enhancement of H_2Y^{2-} acidity in presence of Ba (II), Mg (II) and Ag (I)

The titration curves of 10.0 ml of H_2Y^{2-} in presence of x ml of Ba (II) (0.05 M) from 0 to 25.0 ml are shown in Fig. 2. The titration curve of 10.0 ml of H_2Y^{2-} (0.10 M) alone with NaOH (0.10 M) is compared to the titration of H_2Y^{2-} in presence of metallic ion: the equivalent point shifts to right with increasing x until x = 20.0 ml which corresponds to equal concentration of H_2Y^{2-} and Ba (II) ion. The titration curve for x > 20 ml (like 25 ml) coincides with that of 20.0 ml. The pH at V (NaOH) = 0 shows little decrease since Ba (II) has no action on H_2Y^{2-} due to the small value of equilibrium constant K for the reaction

$$H_2Y^{2-} + Ba\,(II) \rightleftharpoons BaY^{2-} + 2H^+$$

$$K = K_{a1}K_{a2}\beta = 10^{-6.16}.10^{-10.26}.10^{7.8} = 2.210^{-9} << 1$$

During the titration of a mixture of Ba(II) and H_2Y^{2-} against OH^-. Ba (II) binds to liberated HY^{3-} forming BaY^{2-} complex according to:

$$H_2Y^{2-} + OH^- \rightleftharpoons HY^{3-} + H_2O$$

$$HY^{3-} + Ba\,(II) \rightleftharpoons BaY^{2-} + H^+$$

$$HY^{3-} + H^+ \rightleftharpoons H_2Y^{2-}$$

So the global reaction is:

$$2HY^{3-} + Ba\,(II) \rightleftharpoons BaY^{2-} + H_2Y^{2-}$$

$$\text{with } K = \beta.K_{a1}.K_{a2} = 10^{4.4}$$

It is clear that the formation of BaY^{2-} increases H_2Y^{2-} concentration in situ for this reason we have observed a shift for the equivalent point. After the equivalent point, all Ba (II) added has already complexed and any extra addition of NaOH is used to neutralize the remaining HY^{3-}. In order to prove this, we have repeated the titration of H_2Y^{2-} (10 ml) without initial Ba (II). In one experiment, 10.0 ml Ba (II) was added at pH 8.0 which corresponds to the equivalent point of H_2Y^{2-} (100 % HY^{3-}) and in another experiment the 10 ml of Ba (II) was added at the pH 9.8, corresponding to the pKa of HY^{3-} (50 % HY^{3-} , 50 % Y^{4-}). For both cases, when

Table 1. Variation of the initial pH in function of the volume of M (II) added.

Metal ion	pK_c	Initial pH (ml of Metal added)			
		(10 ml)	(15 ml)	(20 ml)	(30 ml)
Ag(I)	7.3	3.64		3.53	
Ba(II)	7.8	4.10	3.96	3.92	3.90
Mg(II)	8.7	3.87	3.78	3.73	

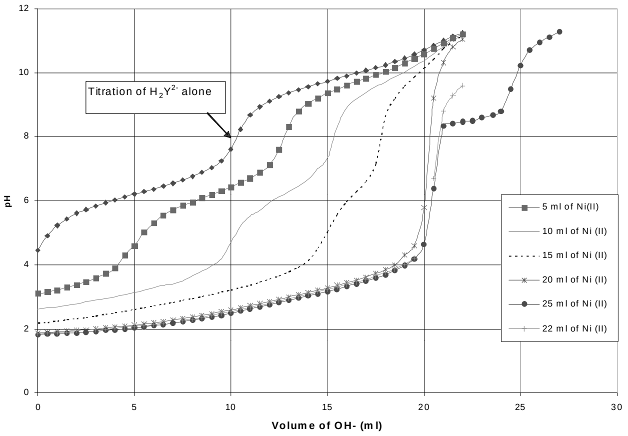

Fig. 5. Titration curves of 10.0 ml of H_2Y^{2-} (0.10 M) in presence of x ml of Ni (II) (0.0505 M) added (x = 10.0, 15.0, 20.0, 25.0 ml).

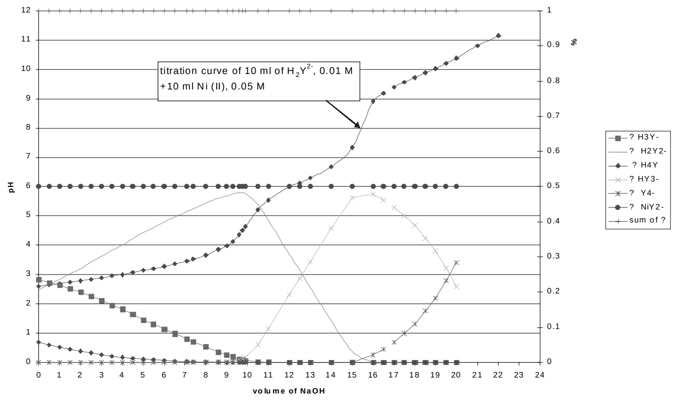

Fig. 6. Variation of the different species of H_4Y versus volume of NaOH (ml) added during the titration of 10.0 ml of H_2Y^{2-} (0.05 M) in presence of 10.0 ml of Ni (II) (0.05 M).

adding Ba (II) the pH dropped suddenly to the same level as if it was added at the start, and then continues perfectly with it. The sudden drop in pH in the first case, can be explained by the quantitative reaction between HY^{3-} and Ba (II) causing the liberation of H^+ as described above. In the second case, complexation of Y^{4-} with Ba (II) causes a decrease in pH. The % curves of important species in solution during titration of 10 ml of H_2Y^{2-} in presence of 10 ml of Ba (II) are shown in Fig. 3. The % curve of H_2Y^{2-} decreases from about 96 % before addition of NaOH (pH = 4.4) to zero at 15 ml of NaOH (pH = 8) accompanied by an increase in HY^{3-} and BaY^{2-}.

The curve of n versus pY^{4-} for Ba (II) (10.0 ml addition) shows a maximum at n = 1 and a pKc = 7.0 The other curves corresponding to different addition of Ba (II) gave the same maximum n value, confirming the formation of only 1:1 BaY^{2-} complex. The pKc obtained experimentally varies between 7.0 and 7.8 with an average equal to 7.3. The previously published value is 7.8 at 20°C and 0.1 M ionic strength [7].

The titration curves of H_2Y^{2-} in presence of Mg (II) (10.0 ml) gave an overall lower titration curve than for Ba (II) due to stronger complexation between Mg (II) and Y^{4-} (Fig. 4) and Table 1. While Ag (I) gave a higher curve than Ba (II) due to weaker complexation. This trends is also for titration with other volume of metal ions added. The pKc obtained by application of Bjerrum's method give 8.2 while the published value is 8.7 [7].

Enhancement of H_2Y^{2-} acidity in presence of Ni (II), Co (II) and Ca (II)

The titration curve of H_2Y^{2-} in presence of any of the title three cations shows simlar trends, Fig. 5. Thus only the titration curve in presence of Ni (II) is discussed. The titration of H_2Y^{2-} in presence of different volume of Ni (II) or Co (II) shows a typical titration curve similar to that for a strong acid, when the metallic ion is present in excess with respect to the concentration of H_2Y^{2-} such as for 20.0 and 25.0 ml of M (II) added. The other curves for 5.0, 10.0 and 15.0 ml of M (II) added correspond to the titration of a mixture of the produced medium strength acids H_3Y^- and H_4Y and the left weak acid H_2Y^{2-} left after complexation, Fig. 5. This is confirmed by the presence of two equivalent points. The first equivalent point corresponds to neutralization of H_4Y and H_3Y^- produced in situ immediately after adding the metallic ion. The second equivalent point corresponds to the neutralization of H_2Y^{2-} left. The shift in the first equivalent point is proportional to the volume of Ni (II) added. By comparison with the titration curve of H_2Y^{2-} in presence of Ba (II), we conclude that the action of Ni (II) on H_2Y^{2-} is different from that of Ba (II). The blue nickel complex is formed when Ni (II) was added before titration with NaOH in contrast to Ba (II) where the complex is formed during titration. This has been confirmed spectrophotometrically. The successive possible reactions for Ni (II) with EDTA before NaOH addition are as follows:

$H_2Y^{2-} + H_2O \rightleftharpoons HY^{3-} + H_3O^+ \quad pK_{a2} = 6.16$

$Ni\,(II) + Y^{4-} \rightleftharpoons NiY^{2-} \quad pKc = 18.6$

The overall reaction is:

$$H_2Y^{2-} + Ni(II) \rightleftharpoons NiY^{2-} + 2H^+$$

$$K = K_{a1}.K_{a2} / K_c = 10^{2.2}.$$

When H_2Y^{2-} is present in excess with respect to Ni (II) the reaction (D) consume all Ni (II). The liberated H^+ will react with H_2Y^{2-} remained in solution according to:

$H_2Y^{2-} + H^+ \rightleftharpoons H_3Y^- \quad K= 1/K_{a3} = 10^{2.7}$

$H_3Y^- + H^+ \rightleftharpoons H_4Y \quad K= 1/K_{a4} = 10^{2}$

The pH of solution will be given by the relation:

$$pH = pK_a(H_3Y^- / H_2Y^{2-}) + \log\frac{[H_3Y^-]}{[H_2Y^{2-}]} = 2.7 + \log\frac{[H_3Y^-]}{[H_2Y^{2-}]}$$

But when Ni (II) is present in excess, the produced H^+ remains free and acts as strong acid. The pH at the equivalent point will be equal 7.0 and the end point volume 20 ml (Fig. 4). Thus adding Ni (II) increases the two successive acidities of H_2Y^{2-}. The effect of complexation of H_2Y^{2-} depends on the type of metallic ions. For example, the pH of H_2Y^{2-} in presence of 25.0 ml of Ba (II) before adding NaOH is about 4 and the pH at the equivalent point is about 9. 9 (corresponding to pH of a weak acid); while these pH in presence of 25.0 ml of Ni (II) are about 2.0 and 7.0, respectively (corresponding to pH of a strong acid) (Fig. 4). Therefore the presence of metallic ions with pKc value < 10 increases only the last acidity of H_2Y^{2-}, and with pKc value >10 increases the two acidities of H_2Y^{2-}.

The reaction between Ni (II) and H_2Y^{2-} is quantitative as confirmed by visible spectroscopic absorbance measurements at 590 nm the λ max of the complex NiY^{2-}. The absorbance of the Ni (II) solution increases linearly with respect to ml H_2Y^{2-} added then remains constant for a concentration of H_2Y^{2-} higher than 1:1 with respect to Ni (II). At higher pH, the precipitates Ni $(OH)_2$ and Co $(OH)_2$ are formed when Co (II) and Ni (II) are present in excess with respect to H_2Y^{2-}, Fig. 5.

$Ni\,(II)$ in excess $+ 2\,OH^- \longrightarrow Ni\,(OH)_2 \quad Ksp = 10^{-16}$

Since NiY^{2-} complex is completely formed before addition of NaOH and its concentration does not vary during titration, Fig. 6, we can not find the pKc of NiY^{2-}. The percentages of other species vary as predicted by the pH of solution and the pK_{ai} of H_4Y. The pKc of Ca (II) has been calculated since the formation of its complex increases during titration. The obtained pKc is 10.1 close to published value 10.8 [7].

CONCLUSIONS

H_2Y^{2-} behaves as strong acid in presence of metallic ions with pKc > 10 such as Co (II) and Ni (II) by increasing the strength its two acidities. While, only the last acidity of H_2Y^{2-} increases in presence of metallic ions with pKc less than 10 such as Ba (II), Mg (II) and silver.

REFERENCES

1. M. Roche, J. Des Barres, C. Cohin, A. Jardy, D. Bauer, Chimie de solutions (Langage et informatique) 1990, p. 179, p.183.
2. F.B. Audat, F. Raffegeau, D. Prevoteau, Chimie Inorganique et gınırale, Dunod, Paris, Second ıdition, 2003, P. 60.
3. J. Mesplede, J.L. Queyrel, Précis de chimie, solutions aqueuses, Breal édition, 1996, p159-160.
4. M.S. Masoud, H.H. Hammud, H. Beidas, Thermochim. Acta, 381, 2002, 119-131.
5. M.J. Zaworototko, H.H. Hammud, I.Abbas, V. Kravtsov, M.S. Masoud, J. Coord. Chem., 2006, 65-84.
6. M. Jaber. Thesis, Lyon, France, 1975, Application de la spectrométrie Infra-Rouge et RAMAN a l'étude des équilibres de complexes en solution.
7. A. Skoog, M. Donald, F. West, James Holler, Chimie analytique 7 éme édition (Bruxelles. De boek 1997).