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The Analytical Investigation for the Use of 1-(2,4 Dinitrophenyl)-4-Ethyl Thiosemicarbazide as an Acid-base Indicator

Amirh AL-Attas

Department of Chemistry, Analytical Chemistry, Girls College of Education,
P.O. Box 16531, Jeddah 21474, Kingdom of Saudi Arabia

Abstract: The pK value (6.60) of the ligand under discussion was calculated from the potentiometric studies. This lower value reflects the relative acidity of the ligand. The stability constants of its complexes were determined and the results in a good agreement with Irving-William series, which supposed that the stability of the complex is coherently attached with the smaller size of the metal ion. The absorption spectra of the ligand at different pHs reveal the two maxima centered at 336 and 450 nm which reflects the presence of the ligand in two forms. The first form appeared in acidic at 336 nm by faint yellow color and the second form in basic medium at 450 nm by red color. From the absorption spectra a relation between pH and the absorbance was drowning, from which the pK value (6.20) was abstracted. This value is in a high agreement with that evaluated potentiometrically. Also, the pH interval value (2.30) was determined by a high value than that known in the literature. This is devoting me to use such compound as an acid-base indicator. This proposed indicator was applied successfully in different acid-base titrations and the results reveal its priority in this field.

Key words: Thiosemicarbazide · acid-base indicator · potentiometric determination

INTRODUCTION

Although ligands having oxygen and nitrogen as donor atoms are by far the most extensively studied, interest in sulfur donor chelating agents has grown over the years and the number of chemical studies in this area has increased considerably [1].

Several areas ranging from general considerations of the effect of sulfur and electron delocalization towards metal ions to potential biological activity and practical application [2-4]. However, little is known about the analytical importance of these ligands. The aim of this work is to know the dissociation constant of 1-(2,4 dinitrophenyl)-4-ethyl thiosemicarbazide and the stability constants of its Co(II), Ni(II), Cu(II),VO^{+2} and Pt(IV) complexes potentiometrically. A chromophoric property of the ligand was discovered accidentally during the potentiometric titrations against NaOH. Such directed me to apply this compound in neutralization titration field.

EXPERIMENTAL

All chemicals used were of analytical reagent grade (BDH) and were used as supplied.

Preparation of the ligand: The equimolar amounts of Ethylisothiocyanate with 2, 4-dinitrophenyl hydrazine were mixed in ethanol and heated under reflux for ~ 2h, after cooling, orange crystals were obtained. The elemental analysis, IR and ^{1}H NMR data proposed the ligand structure.

pH-metric titration: The titration were carried out at 25±1 °C, NaOH was added from burette and the content of the titration vessel was stirred magnetically. The titration was carried out for :

- 2.5 ml HCl (10^{-2} mol L^{-1}) + 1.25 ml KCl (1.0 mol L^{-1}) + 10 ml EtOH.
- 2.5 ml HCl + 1.25 ml KCl + 0.25 ml (10^{-2} mol L^{-1}) ligand + 9.75 ml EtOH.
- Solution b + 0.05 ml (10^{-2} mol L^{-1}) metal ion.
- The above solutions were made up to 25 ml with redistilled water and titrated against 0.99×10^{-2} mol L^{-1} NaOH. The $\bar{n}_A$ is easily calculated applying the Irving and Rossotti equation [5].

$$\bar{n}_A = Y + \frac{(V_1 - V_2)([A]+[B])}{(V_o - V_1)T_L}$$

Corresponding Author: Dr. Amirh AL-Attas, Department of Chemistry, Analytical Chemistry, Girls College of Education, P.O. Box 16531, Jeddah 21474, Kingdom of Saudi Arabia

Where Y is the ionizable proton(s) of the ligand, V_1 and V_2 are the volumes of alkali required to reach the same pH in HCl and in the ligand curves, respectively. V_o is the initial volume of the mixture, T_L is the ligand concentration in the initial volume, [A] and [B] are the concentrations of HCl and NaOH, respectively. The $\bar{n}$ and P_L values were evaluated by the following equations:

$$\bar{n} = \frac{(V_3 - V_2)([A]+[B])}{(V_o + V_1)\bar{n}_A T_M}$$

$$pL = \log \frac{1 + K_1[H^+]}{T_L - \bar{n}\, T_M} \cdot \frac{V_3 V_o}{V_o}$$

for monobasic ligand

Where V_3 is the volume of alkali required to reach the desired pH in the complex solution and T_M is the initial concentration of metal ion.

Procedure for the use of HDNPET as acid-base indicator

Effect of buffer solutions: 0.5 cm^{-1} (10^{-3} mol L^{-1}) from HDNPET was taken in 10 ml measuring flask and completed to the mark with buffer solution having different pHs. The solutions were spectrophotometrically scanned.

Acid-base titrations: 10^{-4} mol L^{-1} concentration of the ligand was used in the titration. Different acids (oxalic, hydrochloric, acetic and boric) were titrated against different concentrations of bases (sodium hydroxide, sodium carbonates and ammonium hydroxide) using one drop of the proposed indicator. The same experiments were carried out using ph.ph. and Me.O indicators for comparison. Different diluted concentrations (10^{-3}, 10^{-4} and 10^{-5} g eq L^{-1}) were prepared and titrated by the same procedure.

Measurements: The infrared spectrum was recorded on a Mattson 5000 FTIR spectrophotometer provided with a CsI beam splitter. The UV/Vis spectra were recorded on a UV/Vis-1601shimadzu spectrophotometer with personal spectroscopy software version 3.7, using 1 cm path length stopper quartz cuvettes. The pH-metric titrations were performed using a Matrohm 744 pH meter (Metrohm, Herisau, Switzerland). The combined glass electrode was standardized using buffer solutions of Metrohm. Carbon and hydrogen content for the ligand were determined at the Microanalytical Unit, Cairo University, Egypt.

RESULTS AND DISCUSSION

Deliberate studies were carried on the ligand under investigation to elucidate its structural and molecular formulae. The elemental analysis showed a high conformity between the found and calculated percentages for the proposed formulae ($C_9H_{11}N_5SO_4$), in which %C= 37.2(calcd.= 37.9), % H= 3.8(calcd.=3.9) and % N= 23.1(calcd.=24.5). The IR spectrum of the ligand shows that, the appearance of three bands at 3241, 3193 and 3150 assigned to $\nu(N^4H)$, $\nu(N^2H)$ and $\nu(N^1H)$ vibrations, respectively and the appearance of two bands at 1247 and 800 cm^{-1} assigned to $\nu_{II}(C{=}S)$ and $\nu_{IV}(C{=}S)$ vibrations. The final tool used in elucidation is ^1H nmr spectrum, which showed the following data; (δ) 3.43 (q, C_2H_5); 7.79 (s, N^4H); 8.25 (m, nitrophenyl); 9.1 (s, N^2HCS-); 9.98(s, N^1H). From all the aforementioned data the structural formulae of the ligand (Fig. 1) was proposed.

pH metric studies: The ionization constants for the organic molecules play an important role. Which are related to the solubility and the extent of binding by a distinguish structure for newly isolated substances. They can be determined through a plot between pH and the average number of protons associated per ligand molecule ($\bar{n}_A$). The first ionization constant (pK) of the ligand was determined by interpolation at $\bar{n}_A$= 0.5 and the second determined at $\bar{n}_A$=1.5. The ligand have only pK value (6.60) assigned for the proton associated with the molecule. The lower value of pK reflected the relative acidity of the molecule. This may refer to the electron withdrawing character for the neighboring group $[(NO_2)_2C_6H_3]$ facilitate the ionization property. The stability constants (Table 1) of the Co(II), Ni(II), Cu(II) VO^{+2} and Pt(IV) complexes in solution were determined. The stability constants ordered as follow Cu(II) > Ni(II) > VO^{+2} > Co(II) this data reveal a good agreement with Irving and Williams [6] series. Pt(IV) complexes showed high stability constants. This is referring to its small size and high charge in comparing with other complexes of divalent metal ions.

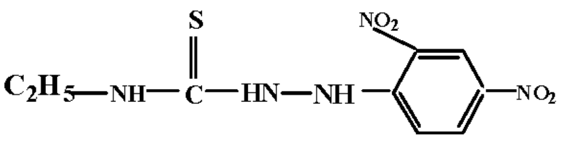

Fig. 1: The structure of HDNPET

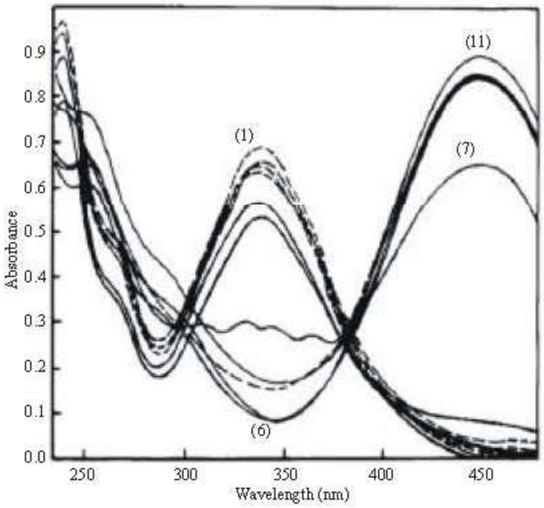

Fig. 2: The effect of pH on the electronic spectra of $5x10^{-5}$ $molL^{-1}$ HDNPET at pH= 2.3(1), 3.1(2), 4.5(3), 5.7(4), 6.8(5), 7.3(6), 8.7(7), 9.8(8), 10.7(9), 11.09(10) and 12.5(11)

The use of HDNPET as an acid-base indicator: Most certified indicators in the neutralization field not covers all titration types especially weak acid-weak base titrations. This referring to the narrow pH interval range (= 2)[7] for most of them, which make each indicator cover defiant type of titration, as ph. Ph. Used in strong bases & weak acids, however, Me.O. in strong acids &weak bases beside strong acid and base. Accordingly, the appearance of new compound acting as indicator covers all titration types successfully. This observation was investigated carefully through the applications.

The absorption spectrum of the compound (Fig. 2) showed two bands centered at 336 and 450 nm. The first band at maximum wave length = 336 nm may assign for the nonionizable form of the compound, which appeared in acidic medium referring to its ionization equation by faint yellow color. The second band at 450 nm assigned for the ionizable form of the compound appeared in basic medium by a red color. The appearance of isosbestic point at 370 nm in the absorption spectra, this point represents the presence of equilibrium between ionizable and nonionizable species [8].

A graphical relation between the pH and their relative absorbance appeared at the two maxima (Fig. 3) was built on the data abstracted from (Fig. 2) The pK value (6.20) of the compound was determined from (Fig. 3), as well as the pH interval (4.9-7.2), which corresponding to 2.3 value. The distinguish behavior of this proposed indicator is expected due to its pH interval value (2.3) which is wider than that of most certified indicators. Also, its behavior is clearly observed from different applications.

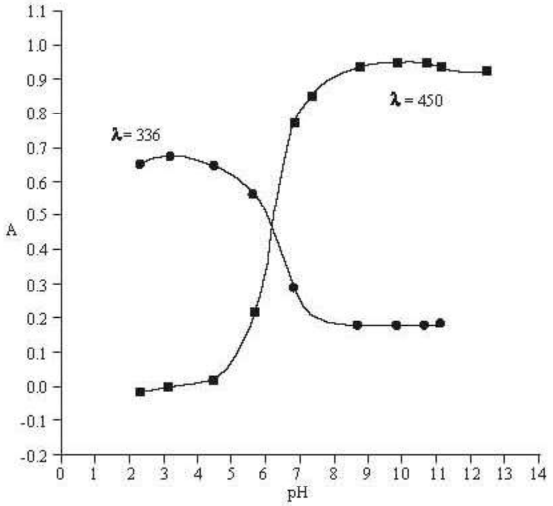

Fig. 3: Absorbance-pH relationship for HDNPET

Table 1: The deprotonation Constant of the Ligand and the Formation Constants of its Complexes β^* is the overall stability const

Compound	pK_1	β_1	β_2	β_3	β^*
HDNPET	6.60	--	--	--	--
Co(II)+ligand	--	5.50	5.10	--	10.60
Ni(II)+ligand	--	5.80	5.60	--	11.40
Cu(II)+ligand	--	6.10	6.10	5.00	17.20
VO(II)+ligand	--	6.20	5.10	--	11.30
Pt(IV)+ligand	--	6.20	6.10	4.95	17.25

β^* is the overall stability const

Strong acid-strong base titrations: Different titrations were carried out on different concentrations from the reactants (HCL and NaOH) using the certified indicators (ph.ph. and Me.O) in comparing with the proposed one. 0.1 g eq L^{-1} is the first concentration used in which the pH titration curve displayed 3-10 as the inflection pH range [9]. This is suitable for the pH interval range of the proposed indicator. The results reveal a high conformity (Table 2) with the known indicators. Low concentrations from the reactants (< 10^{-3} g eq L^{-1}), were used, in which pH titration curve displayed 4.4-8.5, as the inflection pH range. This is suitable for the pH interval of the proposed indicator (4.9-7.2). The priority of new compound appeared with the highly diluted reactants (<5 $x10^{-4}$ g eq L^{-1}).

Weak acid-strong base titrations: 0.1 g eq L^{-1} is the first concentration from HAc as the acid and NaOH used in application, in which the ph. Ph. is the recommended indicator. The results obtained (Table 3) from the proposed indicator and the certified one reveal high conformity. This is due to the presence of pH interval

Table 2: Comparative results and some statistical calculations for HCL and NaOH titration using ph.ph., Me.O and HDNPETS

	HCL, g eq.L^{-1} found			Statistical calculations concerning HDNPETS results			
Taken	Me.O	Ph.ph	HDNPET	A.E.	R.E.	S.	δ
$7x10^{-2}$	$7 x10^{-2}$	$7 x10^{-2}$	$7 x10^{-2}$	0.00	0.00	0.00	0.000
$5.02x10^{-3}$	$5.02x10^{-3}$	$5.02x10^{-3}$	$5.02x10^{-3}$	0.00	0.00	$1.0x10^{-5}$	0.199
$1.05x10^{-3}$	-	$1.05x10^{-3}$	$1.05x10^{-3}$	0.00	0.00	$1.0x10^{-5}$	0.950
$5.00x10^{-4}$	-	$5.00x10^{-4}$	$5.00x10^{-4}$	0.00	0.00	$8.1x10^{-7}$	0.160
$1.10x10^{-4}$	-	-	$1.09x10^{-4}$	$-0.01x10^{-4}$	00.91	$8.1x10^{-7}$	0.740
$9x10^{-5}$	-	-	$9.001x10^{-5}$	$+0.001x10^{-5}$	00.011	$1.52x10^{-8}$	0.017
$7.99x10^{-5}$	-	-	$8.001x10^{-5}$	$+0.011x10^{-5}$	00.137	$8.1x10^{-8}$	0.101

Table 3: Titration of 5 ml from different standardized acids and NaOH (0.07g. eq.L^{-1}) using ph.ph or HDNPETS as indicators

	NaOH (ml)			
Acid, g eq L^{-1}	ph.ph.	HDNPETS	A.E.	R.E.
Oxalic acid, 0.100	4.8	4.8	0.0	0.0
Acetic acid, 0.105	7.5	7.5	0.0	0.0
Phithalic acid, 0.077	5.5	5.5	0.0	0.0

Table 4: Some statistical calculations for weak acid (acetic), weak base (ammonium hydroxidea) titrations

Acetic acid g eq L^{-1}					
Taken	Determined	A.E.	R.E.	S	δ
$1.01x10^{-1}$	$1.01x10^{-1}$	0.00	0.00	$7.07x10^{-4}$	0.70
$1.04x10^{-2}$	$1.03x10^{-2}$	$-1x10^{-4}$	0.96	10^{-4}	0.96
$8.2x10^{-3}$	$8.18x10^{-3}$	$-2x10^{-5}$	0.24	10^{-5}	0.12
$5.9x10^{-3}$	$5.95x10^{-3}$	$+5x10^{-5}$	0.85	$1.4x10^{-5}$	0.24

Table 5: A comparison with some statistical calculations in the determination of boric acid concentration using ph.ph. and HDNPET

Found concentration of boric acid					
Using ph.ph	Using HDNPE	A.E.	R.E.	S	δ
0.1178	0.1176	-0.0002	0.169	0.00017	0.145
0.0120	0.0120	0.0000	0.000	$7.07x10^{-5}$	0.590

range in the middle of pH inflection range (6-11) for such titration [9]. At lower concentration level (10^{-3} g eq L^{-1}), the titration curve displayed a sudden jump at pH range from 6.0 to 8.4 [10], in which the using of ph. Ph. Reveal a high accuracy reaching 99 % [10]. The proposed indicator in such titration reveals accuracy greater than ph.ph.

Strong acid-weak base titrations: A series of titrations was conducted between HCl and NH_4OH using HDNPET as well as the certified indicator (Me.O) for the sake of comparison. The results showed a greatest adaptability between the proposed indicator and the other especially at higher concentrations (=10^{-1} g eq L^{-1}).

Weak acid-weak base titrations: The use of such indicator for detecting this type of titration is considered the essential goal achieved from this study. From the literature, few indicators are the most suitable for this type of titration called mixed indicators. However, the use of these indicators is very tedious also, their storing is not simple. The data summarized in Table 4 the successfully use for the proposed indicator in detecting the Acetic acid-Ammonium hydroxide end point till $4.3x10^{-3}$ g eq L^{-1}. The conformity of the results was observed from some statistical calculations.

Boric acid-Sodium hydroxide titration: A series of titrations was carried out for two concentrations(0.1 and 0.09 g eq L^{-1}) from acid used.The end point of the titration(Table 5) of boric acid & NaOH in presence of ph. Ph. indicator must carried out in presence of glycerol. This is acting as the initiating reagent, lowering the pK of the acid to 9.0 [11] till reaching the ph.ph. interval range. In comparing with the proposed indicator the end point was detected without glycerol by a high accuracy observed from some statistical calculations. The mechanical behavior of the compound in such titration was discussed (Fig. 3).

The proposed mechanism for the indicator during titrations: This is a proposed mechanism (Fig. 4) of the indicator during all titrations except Boric acid titration in which the behavior of the indicator in a different manner. To illustrate the chemical behavior of the compound behind the two different colors in acidic and basic medium. The two indicator theories must be considered to illustrate this mechanism. Bronsted theory which, referring the color obtained in basic medium to the ionization

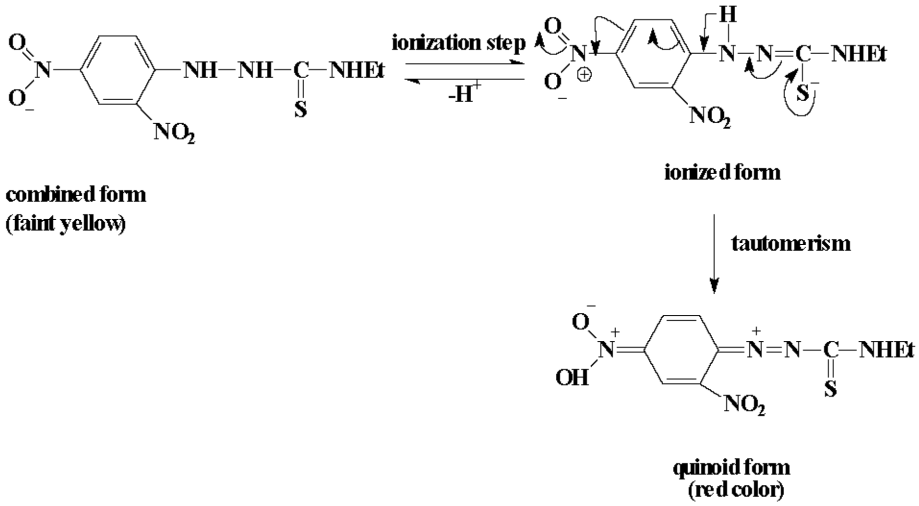

Fig. 4: The proposed mechanism for the behavior of the indicator during titrations

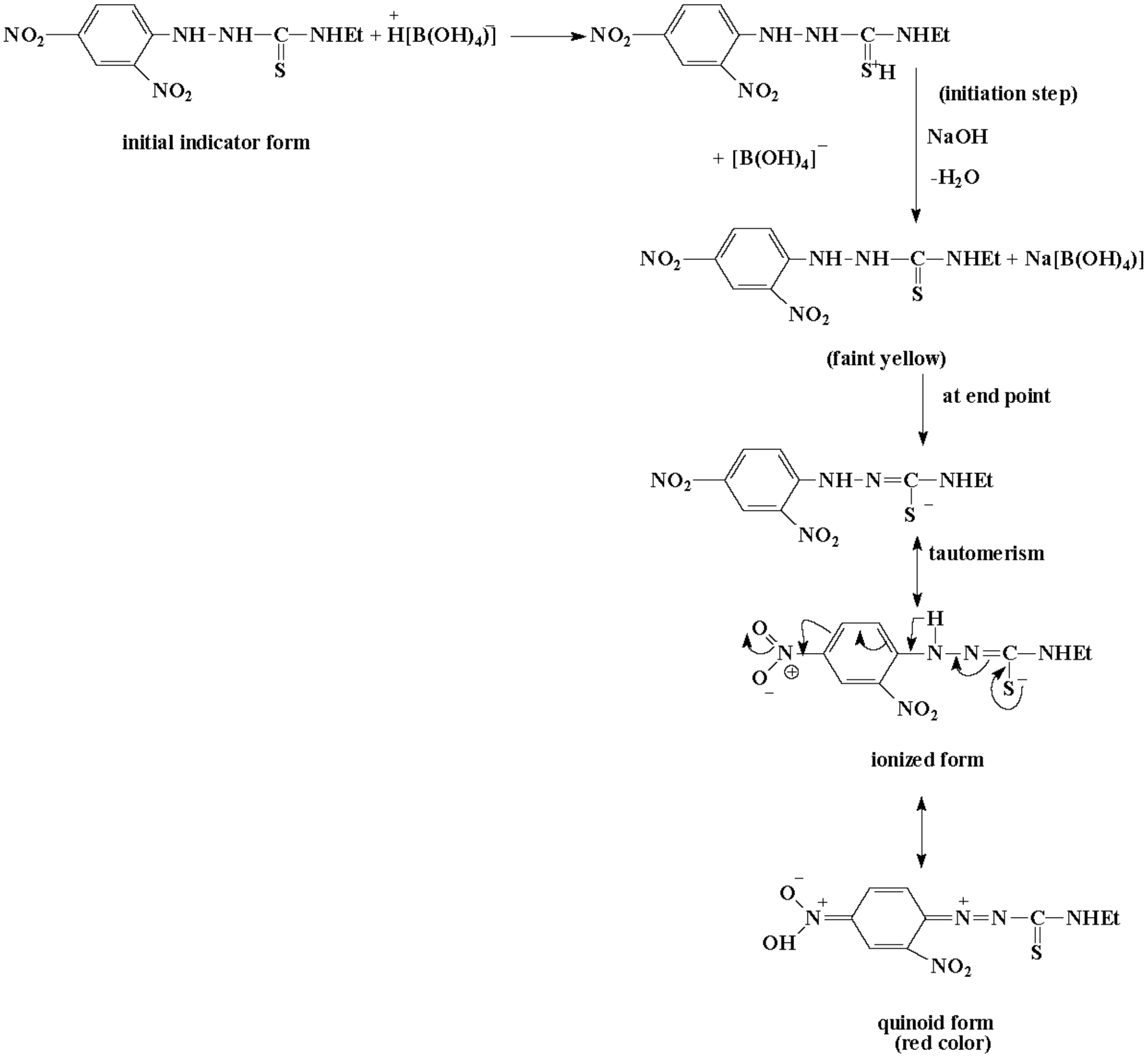

Fig. 5: The proposed mechanism of the indicator in boric acid titration

process for the indicator and the acidic medium reflects the color of indicator in its combined form.

$$\text{H In (combind form)} \rightleftharpoons \text{H}^+ + \text{In}^- \text{ (ionized form)}$$

Chromophor theory is the second theory used to add a final view for the mechanism and referring the color obtained in basic medium to the formation of quiniod or chromophoric structure. Also, the color of organic compound is influenced by the presence of other groups known as auxochromes.

From the first theory the abstracted view reflects a shadow on the ionization site (NH-C=S) in the compound, which acting as the initiated step and propagated through a resonance inside the compound. This steps ended by the formation of quinoid (chromophoric) structure by a dark color in basic medium.

The mechanism of the indication process in boric acid titration: This mechanism (Fig. 5) may be summarized in different points. The first is before the titration process, one or two drops of indicator interacts with equivalence of boric acid and producing free hydrogen ions. The second is during the titration process the liberated protons were consumed by the titrant (NaOH) leading to recreate the indicator original structure. The third is the re obtained indicator molecules stand by for another interaction and the process is continued. On the basis of the data displayed and from the a aforementioned discussion, the hypothetical interaction can be proposed according to series of equations started by the ionization process of boric acid in aqueous solution which takes place as follow:

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+.$$

Such species start the formal process, which described in the Fig. 5:

CONCLUSIONS

The new compound prepared in this study displayed promising results in neutralization field. These results indicate its priority in weak acid-weak base titrations in comparing with the certified indicators as the mixed indicators used for such purpose. Also, its use in normal titrations showed a high conformity with the know indicators but its distinguish appeared in highly diluted solutions. The titration of boric acid in absence of glycerol is the other goal achieved. The mechanical behavior of the proposed indicator was discussed.

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