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Kinetics and mechanism of the reduction of N, N'-salicylideneiminationiron(III) complex ion by L-ascorbic acid in aqueous acid medium

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Abstract

The kinetics and mechanism of the reduction of the iron(III) complex ion, $[FeSalen(H_2O)_2]^+$, by L-ascorbic acid has been investigated in aqueous perchloric acid medium at 28.5 ± 0.3 ^oC. The kinetic data was obtained by monitoring the rate of decay of the complex at 515 nm. Under pseudo-first order conditions of concentration of L-ascorbic acid at about 20-fold excess of concentration of complex, the rate of reaction increased with the concentration of ascorbic acid. Least square fits of observed rate against concentration of ascorbic acid were linear showing first order dependence of rate on concentration of the complex. Also, a plot of $logk_{obs}$ against concentration of ascorbic acid gave a slope of 1.05 implying first order dependence on concentration of ascorbic acid. Second order rate constants were within (31.58 ± 0.50) × 10^{-2} dm^3 mol^{-1} s^{-1}. The rate of reaction increased with increase in the acidity of the medium but was invariant on altering the ionic strength and dielectric constant of the medium. In addition, added CH_3COO^- and Cl^- ions did not affect the rate of reaction. The rate law has been given as;

$$-\frac{1}{2}\frac{d}{dt}\left[FeSalen(H_2O)_2^{+}\right] = k_2[FeSalen(H_2O)_2^{+}][H_2A][H^+]$$

The reaction has been rationalised on the basis of a plausible inner-sphere mechanism.

Key words: L-ascorbic acid, iron(III) complex ion, electron transfer, kinetics, mechanism.

Introduction

A lot of interest has been devoted to the electron transfer reactions of iron[1-5]. This is mainly due to the physiological role played by iron in biological systems[6-8]. In our previous efforts, we had investigated the stoichiometry, kinetics and mechanisms of the reduction of the dinuclear iron(III) complex ion, $[Fe_2\ O]^{4+}$ by L-ascorbic acid[9]. β-meccaptoacetic acid[10], β-mercaptoethanol and mercaptoethylamine[11]. Most of these reactions followed the outer-sphere electron transfer path.

Recently, we have reported the dynamics of the redox reaction of the mononuclear iron(III) complex ion $[FeSalen(H_2O)_2]^+$, with dithionate ion[12]. Based on the kinetic data, the reaction was inferred to be outer-sphere in nature.

Interest in salicylidene Schiff base (Salen) ligands and their complexes revolves around their resemblance of porphyrins[13]. Thus, there is the likelihood that kinetic data obtained with Fe(III)Salen complexes will give an insight into the physiological activity of iron porphyrin enzymes.

L-ascorbic acid is a well known antioxidant[14]. It is physiologically active and is used in medicine in the management of cold symptoms[15]. A compendium of the reactions of ascorbic acid has been published by Davies[16]. However, till date the mechanism of its physiological activity is not well understood.

This report presents the stoichiometry, kinetics and mechanism of the reduction of $[FeSalen(H_2O)_2]^+$ by ascorbic

acid. It is hoped that the results presented herein will give more insight into the interaction of ascorbic acid with particularly Fe(III) porphyrins systems and iron(II) complexes in general.

Experimental

Bis(salicylidene)ethylenediamine (hereafter denoted as Salen) was synthesised and characterised according to literature methods[17, 18]. N,N'-ethylenbis(salicyldeneiminat o) iron(III) complex, $[FeSalen(H_2O)_2]^+$ (hereafter denoted as FeSalen) was prepared following the methods reported by Tanaka *et al*[19]. The ligand and complex were characterized by UV-visible and infrared spectroscopy.

Selected FTIR absorption peaks (nujol, ν/cm^{-1}) for the ligand are: 3424.2 {br, ν(-OH), phenol}; 2996.9-2738.1 (vs, m: ν(aromatic ring); 1637.2 {s, ν (C=N)}; 1530.2 (s, νC-N); UV-Vis(EtOH) λ_{max}/nm; 285, 371, 386. Mp (°C) 125-126, yield: 89%.

Selected FTIR absorption (nujol, ν/cm^{-1}) for the complexes are: 3450 (w, ν(H2O); 2921.34 {s, ν(C-H), aromatic}; 1629.89 {s, ν(C=N)}; 1451.31 {s, ν(C-N)}; 1136-104.46{s,ν(C-O)}; 505 {m, ν(M-O)}, 425 {m, ν(M-N) 248 dec. yield: 92%; UV-Vis(EtOH) λ_{max}/nm; 385, 485, 515 and 710. L-ascorbic acid (Fluka 99.5% Analar) was used as supplied. Reagent grade $HClO_4$ and $NaClO_4$ were used to adjust the acidity and ionic strength of the reaction media respectively doubly. Unless otherwise stated, deionised water was used to prepare all solutions. UV-Vis spectra were recorded in ethanol solution on UNICO-2102 and JENWAY 6405 UV-Vis spectrophotometers. FTIR data of the ligand and complexes were obtained as nujol on Termo Electron Corporation IR 100 Series. Absorbances of the reaction solutions were obtained on Milton Roy Spectronic 21D specetrophotometer.

Kinetic measurements

Rate data for the disappearance of the iron(II) complex in the oxidation of L- ascorbic acid (hereafter H_2A) were obtained as the decrease in the absorbance at 515 nm. At this wavelength, neither the reductant nor the product of the reaction has any significant absorption. The reactions were conducted under pseudo-first-order conditions with the reductant in large excess over the complex. Under such conditions, kinetic curves were exponential and rate constant obtained from logarithmic plot of the absorbance differences (In A_t-A_∞) against time. Pseudo-first-order rate constant were determined from the slope of above plots based on the relation;

$$\text{In } A_t\text{-}A_\infty = k_o t + \text{In } (A_\infty\text{-}A_o)$$

Where A_∞ = final absorbance, A_t = absorbance at time t, A_o = initial absorbance and k_o = pseudo-first-order rate constant as earlier reported[9, 10]. Specific rates for replicate runs are reproducible to within ± 5%.

The presence of free radicals was detected by monitoring gel formation by acrylamide in partial reacted reaction mixture in excess methanol as solvent[9]. The stoichiometry of the reaction was obtained by spectrophotometric titration under the following conditions: Concentration of FeSalen was kept constant at 2.0 X 10^{-4} mol dm^{-3} at $[H^+]$ = 0.001 mol dm^{-3}, I = 0.02 mol dm^{-3} ($NaClO_4$) and concentration of H_2A varied between 2 x 10^{-5} to 3 x 10^{-3} mol dm^{-3} at T = 28.5 ± 0.3 °C. Final absorbances (A∞) of separate reaction solution were plotted against mole ratio. [FeSalen/H_2A] and the stoichiometry derived from the point of inflexion on the curve.

Results and discussion

Following Job's continuous variation method, the metal-ligand mole ratio for the complex was established to be 1:1. Similar result was obtained for the Mn(III) complex of Salen.[20] The electronic and infra red spectral data of the ligand and complex were in accord with other published reports[14-16] and infers that the complex is $[FeSalen(H_2O)_2]^+$in which the metal has octahedral symmetry.

Spectrophotometric titration showed that two moles of $[FeSalen(H_2O)_2]^+$ was consumed for every mole of H_2A oxidized. This observation is in accord with equation (I).

$$H_2A + 2[FeSalen(H_2O)_2]^+ \rightarrow 2[FeSalen(H_2O)_2] + A + 2H^+ \text{ ----------(1)}$$

(A = dehydroascorbic acid)

Similar observations had been noted for most redox reactions of ascorbic acid whereby dehydroascorbic acid is the major organic product of the reaction[16]. The reduction of the Fe(III) complex ion to Fe(II) was confirmed by the reaction of acidified solution of the reaction mixture with freshly prepared potassium hexacyanoferrate(III) as earlier reported[9-12].

Kinetics

Pseudo-first order decays were linear to above 85% extent of reaction indicating first order dependence of rate on concentration of the oxidant. Pseudo-first order and second order rate constants are displayed in Table 1. Variation of initial concentration of L-ascorbic from 5×10^{-3} to 1×10^{-1} mol dm^{-3} at fixed [FeSalen $(H_2O)_2^+$] of 1.010^{-4} mol dm^{-3} with $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.05 mol dm^{-3} ($NaClO_4$) and T = 28.5 ± 0.3 ^oC indicated increase in pseudo-first order rate constant, k_{obs}, with increase in [H_2A] (Table 1). In addition, variation of [FeSalen$(H_2O)_2^+$] between I x10^{-4} to 5 x10^{-4} mol dm^{-3} at constant [H_2A] showed increase in k_{obs} with [FeSalen$(H_2O)_2^+$] (Table 2). These results suggest first order dependence reaction rate on both first oxidant and reluctant. Least square fits (r = 0.988) of logk_{obs} versus log [H_2A] (Figure 1) was linear with a slope of 1.05, which is in agreement with first order dependence of rate of reaction on [H_2A].

Second order rate constants, k_2, were evaluated by dividing k_{obs} by the [H_2A]. k_2 values were fairly constant and at about $(31.58 \pm 0.50) \times 10^{-2}$ dm^{-3} mol^{-1} s^{-1}. Equation (2) represents the rate of reaction based on above results.

$$-\frac{1}{2}\frac{d[FeSalen(H_2O)_2^+}{dt} = k_2[FeSalen(H_2O)_2+][H_2A] \quad \text{----------(2)}$$

Comparism of the rate of reaction with similar reported systems shows that for the reaction of [MnSalen$(H_2O)_2$]$^+$ with H_2A[20], the rate of decomposition of the precursor complex was determined to be 1.50×10^{-2} dm^3 mol^{-1} s^{-1} at 28 ^oC. The authors also determined that the formation of the precursor complex is strongly pH dependent.

In the title reaction, formation of the blue precursor complex was very fast[21, 22] and could not be monitored conventionally using a spectrophotometer. However, the decomposition of the complex leading to electron transfer was rather slow with a k_2 value of $(31.58 \pm 0.50) \times 10^{-2}$. This reaction took place at a relatively low pH of 3.0 which resulted in the preprotonation of ascorbic acid before the formation of the precursor complex. Some workers have reported a linear dependence on ascorbic acid concentration, an inverse dependence on hydrogen ion concentration and excellent pseudo-first order kinetics when ascorbic acid is in large excess over hexacyanoferrate(III) ion for the $H_2A/[Fe(CN)_6]^{3-}$ reaction[21]. For the reaction of some haeme or Fe(III) porphyrin complexes with H_2A, some of the reaction have been shown to be also biphasic at pH 7.0 to pH 8.0[23]. Reduction by the ascorbate of BrCN- modified metmyoglobin and metmyoglobin reconstituted with 2,4-disubstituted deutrohaemin and with protohaemin, dimethyl ester was reported to biphasic where there is a linear correlation between the logarithm of the second order rate constants and the PK_3 of the acid dissociation constants of the porphyrin monocation[24]. Very slow reaction was also inferred for the reaction of ascorbic acid with sperm and whale skeletal muscle myoglobin[25]. There is close conformity of the title reaction with the reaction of the porphyrin complex in terms of the biphasic nature and the slowness of the process even at elevated pH.

Acid dependence

The effect of [H^+] on the reaction kinetics was investigated by varying concentrations of $HC1O_4$ within the range I x 10^{-3} to 4.5×10^{-2} mol dm^{-3} at I = 0.05 mol dm^{-3} ($NaC1O_4$), [H_2A] = 0.01 mol dm^3, [FeSalen$(H_2O)_2]^+ = 1 \times 10^{-4}$ mol dm^{-3} and T = 28.5 ^oC. Under these conditions, the rate of reaction increased with increase [H^+]. The enhancement of the rate of reaction with increase in [H^+] is interpreted to mean a preprotonation step being involved in the reaction. This is likely due to the formation of $[H_3A]^+$ at low pH. Literature report indicated that at pH 6.05 or below the

possibility of formation of H_3A^+ increases and formation of the anion HA^- diminshes[20]. The authors also suggested the remote probability of formation of an intermediate. However, the reduction $[FeSalen(H_2O)_2]^+$ by H_2A indicated the formation of a blue coloured intermediate due to reaction of H_2A^+ with the reductant. This also shows that even at pH 2.0 iron(III) complexes react with H_2A via the formation of a precursor complex. Considering the ease of hydrolysis of the complex[26] (equation 3), the conjugate base could be easily formed at higher pH but its concentration will be diminished at low pH thereby inferring that formation of the intermediate is most likely between $[FeSalen(H_2O)_2]^+$ and H_3A^+.

$$[FeSalen(H_2O)_2]^+ \rightleftharpoons [FeSalen(H_2O)OH] + H^+ \text{ ----------(3)}$$

Acid-dependence rate constants are shown in Table 1. The Plot of k_2 versus $[H^+]$ (Figure 2) gave a linear curve with a positive intercept giving the acid-dependent path of the reaction to be;

$$K_H = a + b\,[H^+] \text{ ----------(4)}$$

Where $a = 31.5 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and

$b = 5.075$ dm^6 mol^{-2} s^{-1}

Effect of ionic strength

Ionic strengths of the reaction media were varied from 0.050 to 0.095 mol dm^{-3} using various portions of $NaClO_4$ at $[FeSalen(H_2O)_2]^+ = 1 \times 10^{-4}$ mol dm^{-3}, $[H_2A] = 0.01$ mol dm^{-3}, T = 28.5^{o}C and λ = 515nm. Results in Table 1 indicate that within the ionic strength range under investigation, the rate of reaction remained invariant. Lack of primary salt effect is indicative of a redox step where the product of changes of the redox partners at the rate determining stage is zero. This behaviour as seen in this reaction is likely due to the fact that at the rate determining steps only the intramolecular election transfer of the precursor complex occurs or a neutrally charged species reacts with the Fe(III) complex as in the following scheme:

$$[FeSalen(H_2O)H_2A]^+ \rightarrow HA + [FeSalenH_2O] + H^+$$

or

$$[FeSalen(H_2O)_2]^+ + HA \rightarrow [FeSalen(H_2O)_2 + A + H^+$$

Effect of dielectric constant (D)

At other parameters kept constant, dielectric constant of the reaction media was varied by adding varying portions of propan-2-one/H_2O mixture. Results in Table 3 show the invariant nature of the observed rate constant as the medium dielectric constant was altered. This is likely the result of redox partners where one is uncharged interacting at the rate determining stage. This observation supports the earlier assertion that the slow process of electron transfer was either intramolecular or involved the uncharged partner. This also indicates that the main reductant species in redox reaction of H_2A are HA and H_2A[20, 27].

Effect of added ions

Catalytic effect of added anions was investigated by adding varying concentrations of chloride and ethanoate ions in the range 0.001 to 0.015 mol dm^{-3}. The results in Table 4 indicate that the rate of reaction was unaffected by adding varying portions of the anions. Lack of anion catalysis in a pointer to likely formation of a precursor complex with inner-sphere character and gives insight to the remoteness of on outer-sphere path[28].

Michaelis-Menten-type plot of $1/k_{obs}$ versus $1/[H_2A]$ (Fig. 3) was linear with intercept thereby implicating operation of an inner-sphere path and likely presence of a preassociation step or presence of intermediate with appreciable equilibrium constant.[27]

Reaction mechanism

With due consideration to the stoichiometry, acid-dependence, effect of ionic strength, effect of dielectric constant, catalysis and Michaelis-Menten-type plot and the fact that the λ_{max} of the reaction changed on scanning the reaction mixture a few seconds into the reaction, the following scheme has been proposed for the reaction:

$$H_2A + H^+ \underset{}{\overset{K}{\rightleftharpoons}} H_3A^+ \text{----------(5)}$$

$$[FeSalen(H_2O)_2]^+ + H_3A^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [FeSalen(H_2A)]^+ + H_3O^+ \text{--(6)}$$

$$[FeSalen(H_2O)(H_2A)]^+ \xrightarrow{k_2} [FeSalen(H_2O)] + HA^* \text{----(7)}$$

$$[FeSalen(H_2O)]H_3O^+ \xrightarrow{k_3} [FeSalen(H_2O)_2] + H^+ \text{----(8)}$$

$$[FeSalen(H_2O)^+ HA^* \xrightarrow{k_4} [FeSalen(H_2O)_2] + A + H^+ \text{------(9)}$$

Rate = $k_2[FeSalen(H_2O)(H_2A^+]^- + k_4[FeSalen(H_2O)_2{}^+][HA^*] \text{----(10)}$

Following steady state approximation,

$$[FeSalen(H_2O)(H_2A^+] = k_1[FeSalen(H_2O)_2{}^+][H_3A^+]$$

$$-k_{-1}[FeSalen(H_2O)(H_2A)^+][H_3A^+] - k_2[FeSalen(H_2O)(H_2A)^+] = 0 \text{-----(11)}$$

$$\Rightarrow [FeSalen(H_2O)(H_2A^+] = \frac{k_1[FeSalen(H_2O)_2{}^+][H_3A^+]}{k_{-1}[H_3O^+] + k_2} \text{----(12)}$$

$$Also[H_3A^+] = K[H_2A][H^+] \text{----(13)}$$

$$[HA^*] = \frac{k_2[FeSalen(H_2O)(H_2A)]}{k_4[FeSalen(H_2O)_2 +]} \text{----------(14)}$$

Substituting equation (12) and (13) into equation (14) gives that

$$[HA^*] = \frac{Kk_1k_2[H_2A][H^+]}{k_4k_2 + [k_4k_{-1}(H_3O)^+]} \text{----------(15)}$$

Substituting equations (12), (13) and (15) into equation (10) gives the rate of reaction as;

$$-\frac{1}{2}\frac{d}{dt}[FeSalen(H_2O)_2^{+}]$$

$$= Kk_1k_2[FeSalen(H_2O)_2^{+}][H_2A]\left(\frac{1}{k_{-1}+k_2}+\frac{[H^+]}{k_2+k_{-1}}\right)----(16)$$

At high $[H^+]$ where $k_2 << [H^+]$, the rate law becomes:

$$rate = Kk_1k_2[FeSalen(H_2O)_2^{+}][H_2A]\left(\frac{1}{k_{-1}}+\frac{[H^+]}{k_2+k_{-1}}\right)----(17)$$

Equation (17) is similar to equation (4) where

$$a = \frac{1}{k_{-2}} \quad and \quad b = \frac{[H^+]}{k_2+k_{-1}}$$

The path followed by the reaction between H_2A and $[FeSalen(H_2O)_2]^+$ can be resolved if the following points are considered;

(a) A plot of $1/k_{obs}$ against $1/[H_2A]$ was linear with negative intercept on the $1/k_{obs}$ axis depicting the formation of a precursor complex of relatively large equilibrium constants.

(b) Absence of catalysis on addition of CH_3COO^- and Cl^- indicates operation of an inner-sphere path and suggests H_2A and HA^- as the main reductant species. Formation of a preassociation complex rules out any available site for attack by anions and hence lack of catalysis.

(c) Formation of a precursor complex was indicated by the rapid formation of a bluish coloured complex which decayed slowly to give a colourless solution. Scanning of the reaction mixture a few seconds into the reaction showed a new λ_{max} centered at 575 nm. Literature reports gave the absorption maxima of closely related complexes at about 560 nm.[16] Above data strongly suggest that the reaction follow inner-sphere electron transfer mechanism in accordance with the proposed reaction scheme.

Table 1 Pseudo-first order and second order rate constants for the reaction of H_2A and $[FeSalen(H_2O)_2]^+$ at $[FeSalen(H_2O)_2]^+ = 1 \times 10^{-4}$ mol dm^{-3}, T = 28.5°C

$[H_2A]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	I (mol dm^{-3})	10^3K_{obs} (s^{-1})	10^2K_2 (dm^{-3} mol^{-1} s^{-1})
0.005	0.001	0.050	1.60	32.00
0.010	0.001	0.050	3.10	31.00
0.050	0.001	0.050	15.10	31.30
0.100	0.001	0.050	32.20	32.20
0.150	0.001	0.050	47.10	31.40
0.010	0.005	0.050	3.51	35.10
0.010	0.015	0.050	3.80	38.00
0.010	0.025	0.050	4.42	44.20
0.010	0.035	0.050	5.01	50.10
0.010	0.045	0.050	5.50	55.00

0.010	0.001	0.055	2.95	29.50
0.010	0.001	0.065	3.10	31.00
0.010	0.001	0.075	3.20	32.00
0.010	0.001	0.085	3.22	32.20
0.010	0.001	0.095	3.31	33.10

Table 2 Rate constants for the reaction of H_2A AND $[FeSalen(H_2O)_2]^+$ AT $[H_2A]$ = 0.01 mol dm^{-3}, I = 0.02 mol dm^{-3}, ($NaClO_4$), $[H^+]$ = 0.01 mol dm^{-3}, λ = 515 nm and T = 28.5 ± 0.3°C.

$10^4[FeSalen(H_2O)_2]^+$ (mol dm^{-3})	10^3K (s^{-1})
1.0	3.90
2.0	4.80
3.0	6.90
5.0	9.60

Table 3 Effect of median dielectric constant (D) on Rate of Reaction of $[FeSalen(H_2O)_2]^+$ and H_2A at $[H_2A]$ = 0.010 and dm^{-3}, $[FeSalen(H_2O)_2]^+ = 1\times10^{-4}$ mol dm^{-3}, λmax = 515 nm and T = 28.5°C.

D	I(mol dm^{-3})	10^3K_{obs} (s^{-1})	10^2K_2 (dm^3 mol^{-1} s^{-1})
72.24	0.050	3.00	30.00
74.40	0.050	3.00	30.00
77.15	0.050	3.30	33.00
80.06	0.050	3.35	33.50

Table 4 Effect of added Cl^- and CH_3COO^- ions on the rate of $[FeSalen(H_2O)_2]^+$ and H_2A reaction at $[H_2A]$ = 0.010 mol dm^{-3} $[FeSalen(H_2O)_2]^+ = 1\times10^{-4}$ mol dm^{-3}, λmax = 515 nm, T = 28.5°C, I = 0.050 mol dm^{-3} ($NaClO_4$), $[H^+]$ = 0.00 mol dm^{-3} ($HClO_4$)

$[Cl^-]$ (mol dm^{-3})	10^3 K_{obs} (s^{-1})	10^2K_2 (dm^3 mol^{-1} s^{-1})
0.001	2.98	29.80
0.003	2.95	2950
0.005	3.10	31.00
0.008	3.15	31.50
0.010	3.00	30.00
0.015	3.12	31.20
$[CH_3COO^-]$		
0.001	3.12	31.20
0.003	3.15	31.50
0.005	3.10	31.00
0.008	2.78	27.80
0.010	3.12	31.20
0.015	2.88	28.80

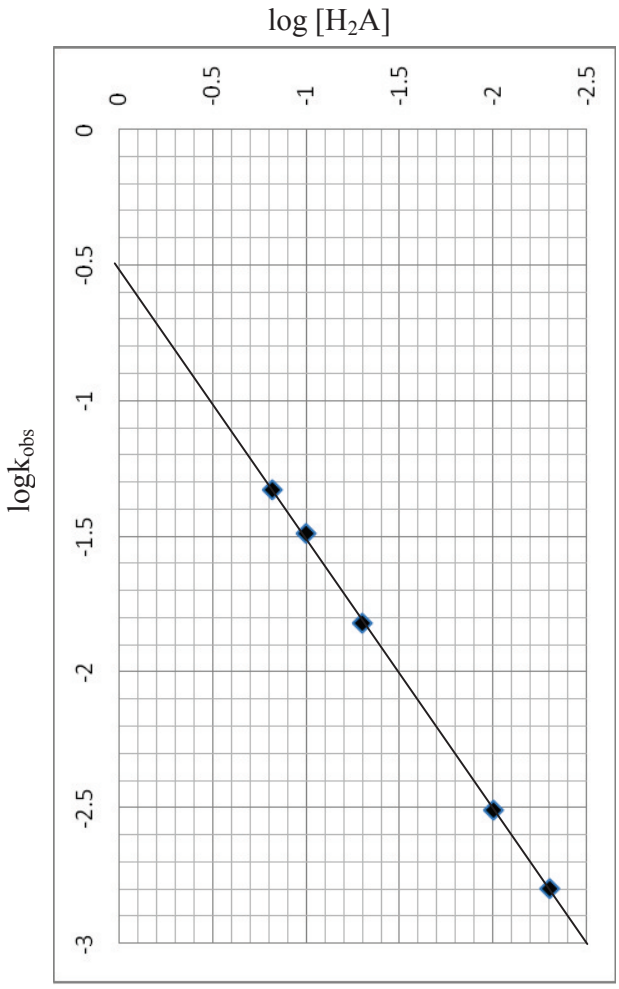

Figure 1 Graph of log [H_2A] vs $logk_{obs}$

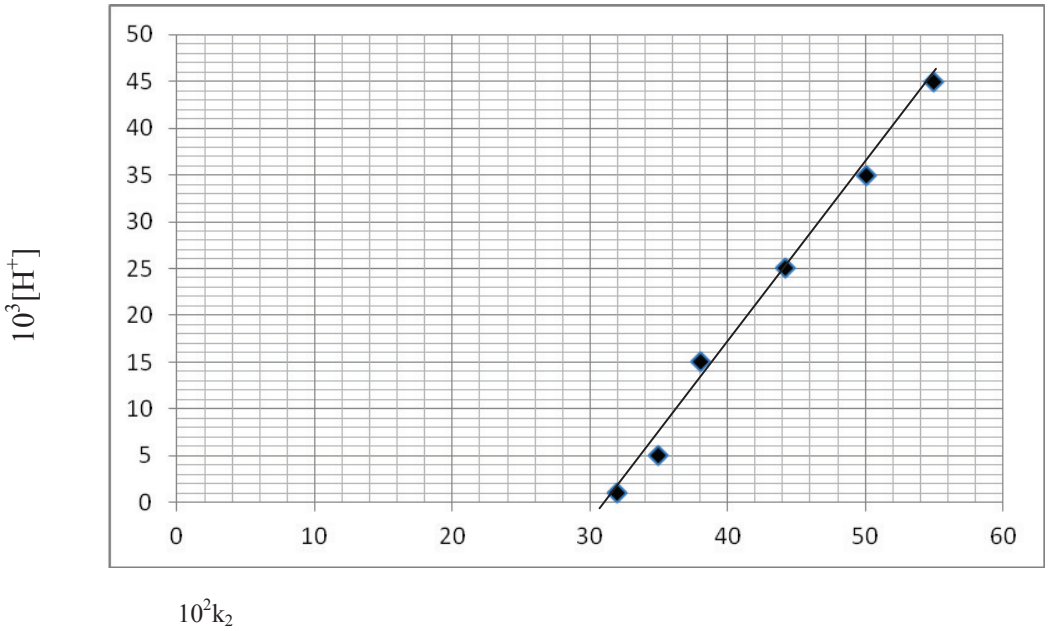

Figure 2 Graph of 10^2k_2 vs $10^3[H^+]$

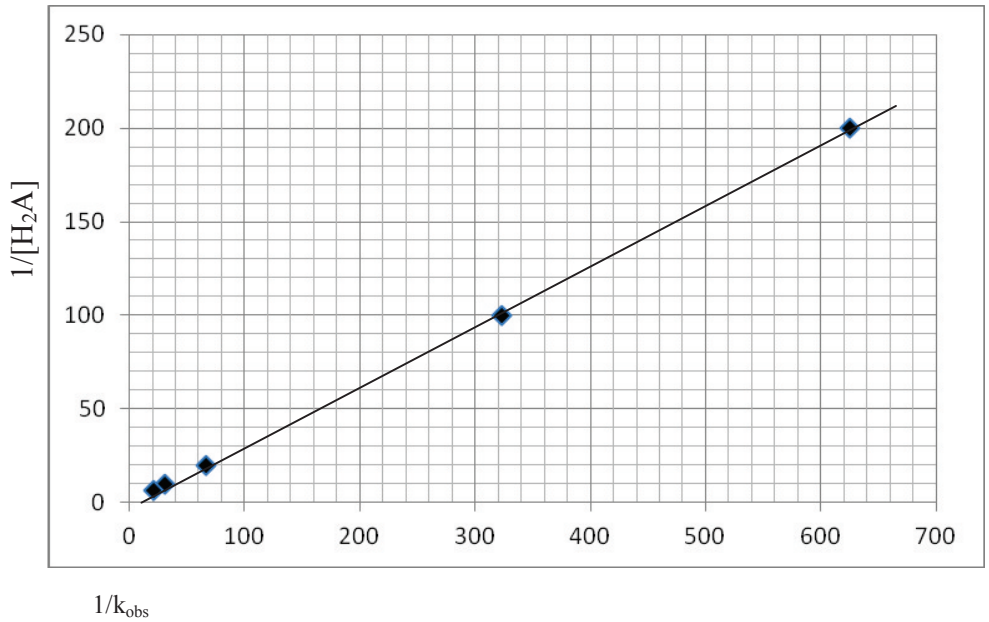

Figure 3 Graph of $1/K_{obs}$ vs $1/[H_2A]$

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