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# Kinetic Study For The Reactions Of Paracetamol With Diazotized (P-Nitroaniline & Sulfanilic Acid Sodium Salt) Reagents

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**Abstract**

The kinetic reactions were studied for formation of colored complexes derived from the electron-donating paracetamol with the two diazotized reagents: (sulfanilic acid sodium salt) and (para-nitro aniline) accepting these electrons at a temperature of (25°C) and at different pH . The formation kinetics of the above complexes was followed spectrophotometrically at the optimal conditions for each of them, after determining the optimal mole ratios for the concentrations of the components of each complex, which were (1:10) for (drug: reagent), respectively. And our current study proved that these interactions are Pseudo-first-order relative to the paracetamol drug. We were able to calculate the rate constant for the formation of the two produced compounds ($k_1$). The highest value for the compound (Paracetamol Drug+Diazotized Sulfanilic Acid Sodium Salt) is (0.0328 $min^{-1}$ at pH9.2), and for the compound (Paracetamol Drug +Diazotized para-Nitro Aniline) is (0.0305 $min^{-1}$ at pH9.2). We also calculated the half-life-time ($t_{1/2}$) for each of them, and it was (21.1min.) and (22.7min.), respectively, which is completely opposite to the values of their rate constants under the same conditions.

*Keywords:* paracetamol, drug complexes, rate constant, Pseudo-first-order, effect of pH.

## 1. Introduction

Paracetamol[1-4] or acetaminophen, which is the name adopted in the United States (English: Acetaminophen), is a widely used analgesic and antipyretic. It is extracted from tar, which is the active metabolite of phenacetin, and unlike phenacetin, paracetamol has not been shown to be carcinogenic in any way. Paracetamol does not have many side effects. It is generally used to treat fever, headache, pain and mild aches. Paracetamol is also useful for other severe pain in combination with NSAIDs or opioid analgesics. NSAIDs are pain relievers (such as aspirin, ibuprofen, ketoprofen, naproxen sodium) and are used to remove or temporarily relieve pain and headache. Paracetamol is an essential ingredient in many cold and flu recipes. Although it is safe for humans within the recommended dose limits, excessive doses can cause hepatotoxicity; The risk increases by drinking alcoholic beverages. Paracetamol side effects: low fever with nausea, stomach pain, and loss of appetite; dark urine, clay-colored stools; or jaundice (yellowing of the skin or eyes). The word acetaminophen is derived from the chemical name of the compound: para-acetyl-para-aminophenol, as well as the word para-acetaminophen. In some contexts, it may be abbreviated to APAF from N-Acetyl-Para-Aminophenol[1-4]. Diazonium salts are an important chemical compound for the preparation of many organic compounds, including the colored phenolic azo-imine complexes. It is prepared from the reaction of primary aromatic amines with nitrous acid and the treatment of sodium nitrite with amine solution in hydrochloric acid at a low temperature (0-5ºC)[5-10]. As for our current research, it included the determination of the reaction order and finding rate constants and half-life time for the reaction of formation of aromatic azodyes derived from the electron-donating drug paracetamol with two different diazotized reagents accepting those electrons at different acidic functions (pH) and constant temperature (25°C).

## 2. Experimental

### *2.1. Chemicals*

The chemicals used during the research were supplied by Switzerland Fluka, British BDH and Spanish PRS companies: sodium hydroxide, hydroxylamine hydrochloride, ethanol, sodium carbonate, sodium nitrite, hydrochloric acid, sulfanilic acid sodium salt, and para-nitro-aniline. While Paracetamol drug got from the Nineveh Drug Company (NDI), Iraq. All compounds were prepared

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in a standard manner similar to a previous study [5, 11-16].

### *2.2. Instruments*

#### *2.2.1. UV-Visible Spectrophotometers*

In this research, I used two spectrophotometers, the first is a single beam Spectrophotometer an instrument manufactured by the British company (Cecil) (Cambridge, England) model (CE 1011/1000) in the range of wavelengths (325-1000nm.). And the second is a double beam Spectrophotometer an instrument containing a computer made by the Japanese company (Shimadzu), model (UV-1800) produced in 2004 to check the value of ($\lambda_{max}$) for the complexes understudy and draw the different electronic spectra in the water solvent in the range between (190-1100nm.). The cells used above were: glass in the visible region and quartz in the Ultra Violet (U.V.) region.

#### *2.2.2. pH-meter*

Made by (JENWAY) Company, Model (3510). Before starting the use of the pH-meter, we calibrated it using international standard solutions: (pH4), (pH7) and (pH9).

#### *2.2.3. Water bath*

Model (D3165) type (Hanigsen) manufactured by (KOTTERMANN) company.

#### *2.2.4. Preparation of the aqueous paracetamol solution*

The drug was obtained pure in the form of a white crystalline powder from the Nineveh Drug Company, and it was used directly to prepare its aqueous paracetamol solution at the concentration of ($10^{-3}$M), to be subsequently reacted with the aqueous solutions of two diazotized reagents (sulfanilic acid sodium salt) and (para-nitro aniline).

#### *2.2.5. Preparation of the diazotized reagent solutions[5-10]*

They were prepared at the concentration of($10^{-3}$M) from each of the diazonium salt derived from sulfanilic acid and derived from para-nitro aniline according to the standard method found in the literature[5-10] , and was applied spontaneously each time.

#### *2.2.6. Preparation of the basic salt solution*

A base salt solution of sodium carbonate at the concentration of (0.1M) was prepared by standard methods[12-16] , to be used later to adjust the acidic functions of the solutions of the paracetamol complexes understudy at the required values (pH4.8, pH7.2 and pH9.2). In the laboratory, different volumes of sodium carbonate solution were added to both reagents and pharmaceutical solutions to obtain the required acidic medium (pH), because part of the carbonate salt was expected to convert to carbonic acid due to the presence of hydrochloric acid with the solutions of reagents. Thus, a mixture of weak carbonic acid and its salt is formed, which serves as a buffer solution to control the pH.

#### *2.2.7. Preparation of the drug complexes solutions[5-6]*

The aqueous solutions of the two paracetamol complexes were prepared under optimal conditions previously obtained, by mixing appropriate quantities of($10^{-3}$M) from the diazotized reagent and (0.1M) from the carbonate salt solution with (0.2ml) of ($10^{-3}$M) from the paracetamol solution at a temperature of(25°C) to obtain the required acidic functions : (pH4.8, pH7.2 and pH9.2).

#### **2.2.8.The Kinetic Study[17-20]**

The mixture of the solutions mentioned above was fixed each time at the selected temperature (25°C). As the aqueous solutions of the two drug complexes were prepared according to the optimum order of addition, as shown in Table (1). The absorption of each kinetic complex was followed at its optimum wavelength and until the end of the reaction or reaching its maximum value ($\lambda_{max}$). The kinetic equation was applied for Pseudo-first-order reaction, and the velocity constant (k), half-life ($t_{1/2}$) as well as other activation parameters were calculated.

## 3. Results and Discussion

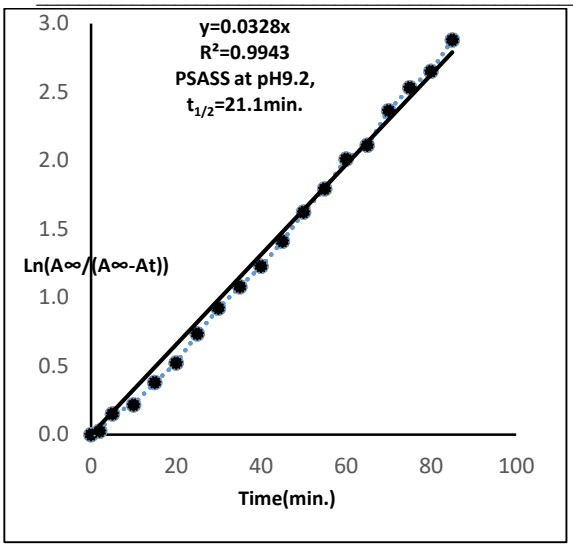
In this study, we relied on previous studies[5-6] which included the best optimal conditions for the formation of the two compounds derived from the reaction of salicylic acid drug one time with diazotized para-nitroaniline reagent and the other with diazotized sulfanilic acid sodium salt reagent which was represented by setting: best primitive wavelength, optimum volume of the reagent, The suitable concentration of the base salt to control the pH function, the optimum order of addition, and, therefore, the final optimum wavelength ($\lambda_{max}$) of the produced complex under optimal conditions. As well as other previous studies[7-9, 12-19] that included the same procedure with replacing the drug with imine, Schiff base or oxime. In our research, we confirmed that the UV and visible spectrum of the two drug complexes, as shown in Table(1), showed spectral ranges with a values of ($\lambda_{max}$), and final optimal coditions as shown in Table(1). These results confirm that there is no spectral interference between the resulting complex and the reactants. Accordingly, this kinetic spectroscopy study was based on the kinematic equation model of the first order in following up the formation of the formed drug complex, by following up the absorption of the resulting complex to a time exceeding (120) minutes. And as shown in Table (2) and Figure (1).

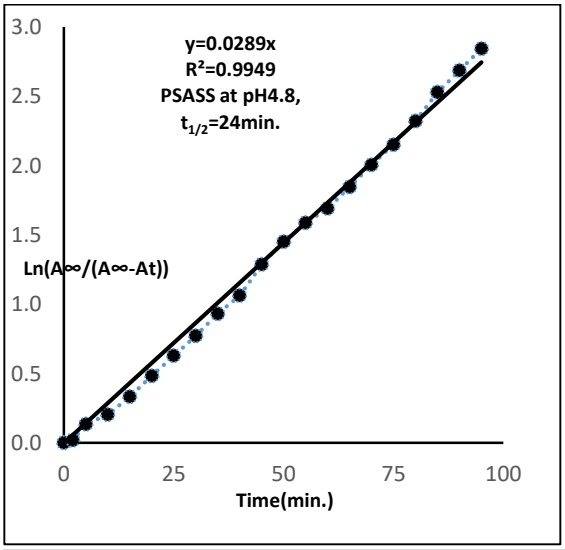
Table 1:**The final optimum conditions for the two prepared paracetamol complexes are understudy at a temperature of (25°C) and at (pH4.8, pH7.2 and pH9.2).**

| Symb. And Name of Complex | Optimum Order of Addition | | Optimum Wavelength (nanometer) |
|---|---|---|---|
| (PSASS) Paracetamol Drug + Diazotized Sulfanilic Acid Sodium Salt | pH4.8 | 0.2ml($10^{-3}$M of paracetamol)+ 2.0ml($10^{-3}$M of diazotized reagent)+ 0.05ml(0.1M of sodium carbonate). | 433 |
| | pH7.2 | 0.2ml($10^{-3}$M of paracetamol)+ 2.0ml($10^{-3}$M of diazotized reagent)+ 0.15 ml(0.1M of sodium carbonate ). | 425 |
| | pH9.2 | 0.2ml($10^{-3}$M of paracetamol)+ 2.0ml($10^{-3}$M of diazotized reagent)+ 0.25 ml(0.1M of sodium carbonate ). | 419 |
| (PPNA) Paracetamol Drug + Diazotized para-Nitro Aniline | pH4.8 | 2.0ml($10^{-3}$M of diazotized reagent)+ 0.2ml($10^{-3}$M of paracetamol)+ 0.15 ml(0.1M of sodium carbonate ) | 439 |
| | pH7.2 | 0.3 ml(0.1M of sodium carbonate)+ 2.0ml($10^{-3}$M of diazotized reagent)+ 0.2ml($10^{-3}$M of paracetamol). | 434 |
| | pH9.2 | 0.6 ml(0.1M of sodium carbonate )+ 2.0ml($10^{-3}$M of diazotized reagent)+ 0.2ml($10^{-3}$M of paracetamol). | 425 |

Table 2: **Monitoring complex(PSASS) absorption versus time at a temperature of (25°C), at (pH4.8, pH7.2 and pH9.2), and at the optimum wavelength for each of pH.**

| Time (min) | Absorption | | | $A_\infty$-$A_t$ | | | $A_\infty$/( $A_\infty$-$A_t$) | | | Ln {$A_\infty$/( $A_\infty$-$A_t$)} | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pH4.8, $\lambda_{max}$= 433 nm | pH7.2, $\lambda_{max}$= 425 nm | pH9.2, $\lambda_{max}$= 419 nm | pH4.8 | pH7.2 | pH9.2 | pH4.8 | pH7.2 | pH9.2 | pH4.8 | pH7.2 | pH9.2 |
| 0 | 0.000 | 0.000 | 0.000 | 0.602 | 0.815 | 0.553 | 1.00 | 1.00 | 1.00 | 0.000 | 0.000 | 0.000 |
| 2 | 0.011 | 0.021 | 0.013 | 0.591 | 0.794 | 0.540 | 1.02 | 1.03 | 1.02 | 0.018 | 0.026 | 0.024 |
| 5 | 0.076 | 0.082 | 0.077 | 0.526 | 0.733 | 0.476 | 1.14 | 1.11 | 1.16 | 0.135 | 0.106 | 0.150 |
| 10 | 0.111 | 0.119 | 0.108 | 0.491 | 0.696 | 0.445 | 1.23 | 1.17 | 1.24 | 0.204 | 0.158 | 0.217 |
| 15 | 0.171 | 0.178 | 0.175 | 0.431 | 0.637 | 0.378 | 1.40 | 1.28 | 1.46 | 0.334 | 0.246 | 0.380 |
| 20 | 0.231 | 0.238 | 0.225 | 0.371 | 0.577 | 0.328 | 1.62 | 1.41 | 1.69 | 0.484 | 0.345 | 0.522 |
| 25 | 0.281 | 0.291 | 0.288 | 0.321 | 0.524 | 0.265 | 1.88 | 1.56 | 2.09 | 0.629 | 0.442 | 0.736 |
| 30 | 0.324 | 0.333 | 0.333 | 0.278 | 0.482 | 0.220 | 2.17 | 1.69 | 2.51 | 0.773 | 0.525 | 0.922 |
| 35 | 0.365 | 0.375 | 0.365 | 0.237 | 0.440 | 0.188 | 2.54 | 1.85 | 2.94 | 0.932 | 0.616 | 1.079 |
| 40 | 0.394 | 0.403 | 0.391 | 0.208 | 0.412 | 0.162 | 2.89 | 1.98 | 3.41 | 1.063 | 0.682 | 1.228 |
| 45 | 0.436 | 0.441 | 0.418 | 0.166 | 0.374 | 0.135 | 3.63 | 2.18 | 4.10 | 1.288 | 0.779 | 1.410 |
| 50 | 0.461 | 0.477 | 0.444 | 0.141 | 0.338 | 0.109 | 4.27 | 2.41 | 5.07 | 1.451 | 0.880 | 1.624 |
| 55 | 0.479 | 0.495 | 0.461 | 0.123 | 0.320 | 0.092 | 4.89 | 2.55 | 6.01 | 1.588 | 0.935 | 1.794 |
| 60 | 0.491 | 0.516 | 0.479 | 0.111 | 0.299 | 0.074 | 5.42 | 2.73 | 7.47 | 1.691 | 1.003 | 2.011 |
| 65 | 0.507 | 0.542 | 0.486 | 0.095 | 0.273 | 0.067 | 6.34 | 2.99 | 8.25 | 1.846 | 1.094 | 2.111 |
| 70 | 0.521 | 0.561 | 0.501 | 0.081 | 0.254 | 0.052 | 7.43 | 3.21 | 10.63 | 2.006 | 1.166 | 2.364 |
| 75 | 0.532 | 0.581 | 0.509 | 0.070 | 0.234 | 0.044 | 8.60 | 3.48 | 12.57 | 2.152 | 1.248 | 2.531 |
| 80 | 0.543 | 0.601 | 0.514 | 0.059 | 0.214 | 0.039 | 10.20 | 3.81 | 14.18 | 2.323 | 1.337 | 2.652 |
| 85 | 0.554 | 0.615 | 0.522 | 0.048 | 0.200 | 0.031 | 12.54 | 4.08 | 17.84 | 2.529 | 1.405 | 2.881 |
| 90 | 0.561 | 0.633 | 0.553 | 0.041 | 0.182 | 000 | 14.68 | 4.48 | ∞ | 2.687 | 1.499 | - |
| 95 | 0.567 | 0.651 | 0.519 | 0.035 | 0.164 | 0.034 | 17.20 | 4.97 | 16.26 | 2.845 | 1.603 | 2.789 |
| 100 | 0.602 | 0.677 | 0.499 | 000 | 0.138 | 0.054 | ∞ | 5.91 | 10.24 | - | 1.776 | 2.326 |
| 105 | 0.597 | 0.691 | 0.471 | 0.005 | 0.124 | 0.082 | 120.40 | 6.57 | 6.74 | 4.791 | 1.883 | 1.909 |
| 110 | 0.548 | 0.701 | 0.452 | 0.054 | 0.114 | 0.101 | 11.15 | 7.15 | 5.48 | 2.411 | 1.967 | 1.700 |
| 115 | 0.522 | 0.815 | 0.443 | 0.080 | 0.000 | 0.110 | 7.53 | ∞ | 5.03 | 2.018 | - | 1.615 |
| 120 | 0.444 | 0.444 | 0.409 | 0.158 | 0.371 | 0.144 | 3.81 | 2.20 | 3.84 | 1.338 | 0.787 | 1.346 |



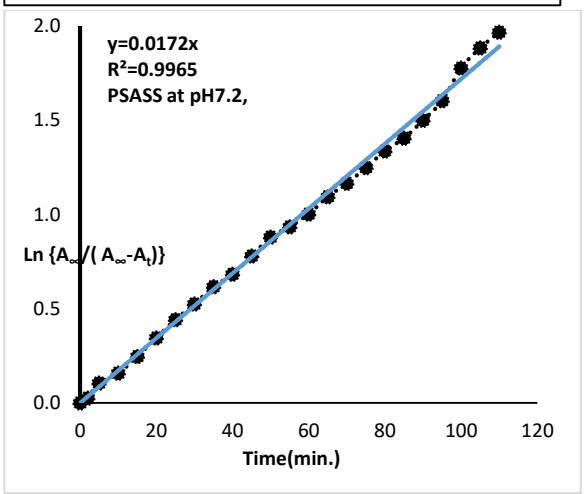




**Figure 1**
**Kinetic of complex(PSASS) absorption versus time at a temperature of (25°C), at (pH4.8, pH7.2 and pH9.2), and at the optimum wavelength for each of pH.**

Figure(1) shows that there is a direct relationship between the absorptions of the complex(PSASS) with time. It was also noticed that there was a sudden decrease in the aforementioned absorptions after (100) minutes after the formation of the drug complex at (pH4.8), after (115) minutes after the formation of the drug complex at (pH7.2), and after (90) minutes after the formation of the drug complex at (pH9.2), and then the absorption to a stable state may be due to the completion of complex formation and the termination of the reaction. And the latter does not affect the values of ($\lambda_{max}$) of the complex formed after these times, due to the end of the reaction, and this is confirmed by the values of the half-life times of its reactions, which were: (24min. at pH4.8), (40.3min. at pH7.2) and (21.1min. at pH9.2).

In this study, we used the integration method to follow the kinetics of complex formation reactions. When applying for the following Pseudo-first-order equation to all the obtained kinetic results:

**$Ln\{A_\infty/(A_\infty-A_t)\}= k1.t$ ----------(1)**

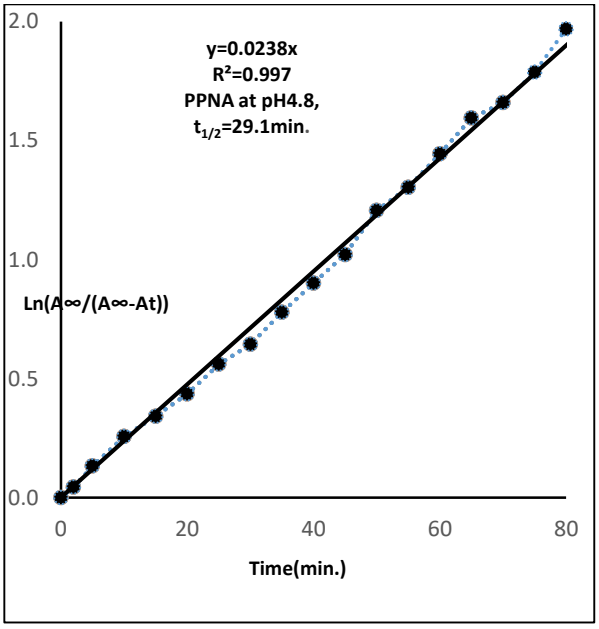
And by plotting **$Ln\{A_\infty/(A_\infty-A_t)\}$** graph against time (in minutes), we got good straight lines at all pH functions with values ($R^2$) between (0.9943-0.9965) with slopes equal to the velocity constants (k). ) Their interactions, the latter indicates that the drug complex formation reaction is of Pseudo-first-order relative to the drug. From them, the velocity constants of the complex formed at the three acidic functions and at a temperature (25°C) were calculated, which enabled us to calculate the values of its half-life time ($t_{1/2}$), which were calculated from the following second equation: (24min. at pH4.8), (40.3min. at pH7.2) and (21.1min. at pH9.2).

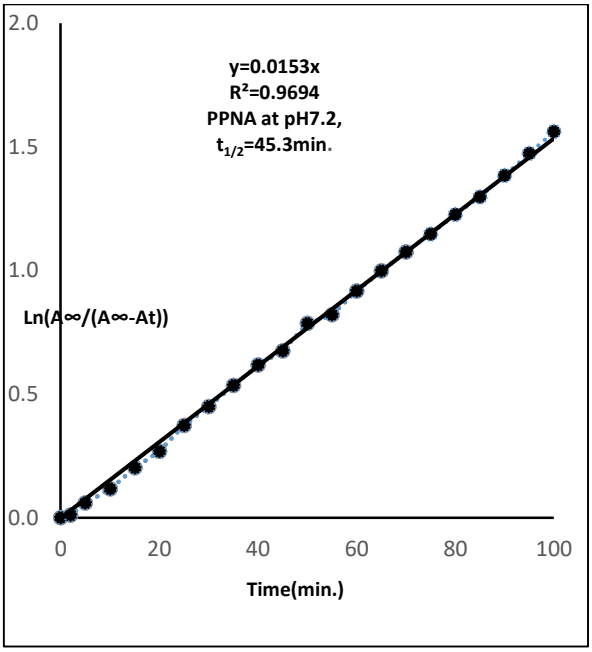
**$t_{1/2}=Ln2/k_1$----------(2)**

These results were identical to previous studies [20-22] on the kinetics of the reaction of the formation of Azo complexes.

**Table 3**
**Monitoring complex(PPNA) absorption versus time at a temperature of (**25°C**), at (pH4.8, pH7.2 and pH9.2), and at the optimum wavelength for each of pH.**

| Time (min) | pH4.8, $\lambda_{max}$= 439 nm | pH7.2, $\lambda_{max}$= 434 nm | pH9.2, $\lambda_{max}$= 425 nm | $A_\infty$-$A_t$ pH4.8 | $A_\infty$-$A_t$ pH7.2 | $A_\infty$-$A_t$ pH9.2 | $A_\infty$/( $A_\infty$-$A_t$) pH4.8 | $A_\infty$/( $A_\infty$-$A_t$) pH7.2 | $A_\infty$/( $A_\infty$-$A_t$) pH9.2 | Ln {$A_\infty$/( $A_\infty$-$A_t$)} pH4.8 | Ln {$A_\infty$/( $A_\infty$-$A_t$)} pH7.2 | Ln {$A_\infty$/( $A_\infty$-$A_t$)} pH9.2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.394 | 0.838 | 0.359 | 1.00 | 1.00 | 1.00 | 0.000 | 0.000 | 0.000 |
| 2 | 0.017 | 0.009 | 0.019 | 0.377 | 0.829 | 0.340 | 1.05 | 1.01 | 1.06 | 0.044 | 0.011 | 0.054 |
| 5 | 0.049 | 0.048 | 0.052 | 0.345 | 0.790 | 0.307 | 1.14 | 1.06 | 1.17 | 0.133 | 0.059 | 0.156 |
| 10 | 0.089 | 0.092 | 0.092 | 0.305 | 0.746 | 0.267 | 1.29 | 1.12 | 1.34 | 0.256 | 0.116 | 0.296 |
| 15 | 0.114 | 0.153 | 0.112 | 0.280 | 0.685 | 0.247 | 1.41 | 1.22 | 1.45 | 0.342 | 0.202 | 0.374 |
| 20 | 0.139 | 0.197 | 0.137 | 0.255 | 0.641 | 0.222 | 1.55 | 1.31 | 1.62 | 0.435 | 0.268 | 0.481 |
| 25 | 0.169 | 0.261 | 0.164 | 0.225 | 0.577 | 0.195 | 1.75 | 1.45 | 1.84 | 0.560 | 0.373 | 0.610 |
| 30 | 0.187 | 0.303 | 0.181 | 0.207 | 0.535 | 0.178 | 1.90 | 1.57 | 2.02 | 0.644 | 0.449 | 0.702 |
| 35 | 0.213 | 0.347 | 0.209 | 0.181 | 0.491 | 0.150 | 2.18 | 1.71 | 2.39 | 0.778 | 0.535 | 0.873 |
| 40 | 0.234 | 0.386 | 0.232 | 0.160 | 0.452 | 0.127 | 2.46 | 1.85 | 2.83 | 0.901 | 0.617 | 1.039 |
| 45 | 0.252 | 0.411 | 0.251 | 0.142 | 0.427 | 0.108 | 2.77 | 1.96 | 3.32 | 1.021 | 0.674 | 1.201 |
| 50 | 0.276 | 0.456 | 0.282 | 0.118 | 0.382 | 0.077 | 3.34 | 2.19 | 4.66 | 1.206 | 0.786 | 1.540 |
| 55 | 0.287 | 0.469 | 0.299 | 0.107 | 0.369 | 0.060 | 3.68 | 2.27 | 5.98 | 1.304 | 0.820 | 1.789 |
| 60 | 0.301 | 0.503 | 0.309 | 0.093 | 0.335 | 0.050 | 4.24 | 2.50 | 7.18 | 1.444 | 0.917 | 1.971 |
| 65 | 0.314 | 0.529 | 0.317 | 0.080 | 0.309 | 0.042 | 4.93 | 2.71 | 8.55 | 1.594 | 0.998 | 2.146 |
| 70 | 0.319 | 0.552 | 0.322 | 0.075 | 0.286 | 0.037 | 5.25 | 2.93 | 9.70 | 1.659 | 1.075 | 2.272 |
| 75 | 0.328 | 0.572 | 0.359 | 0.066 | 0.266 | 0.000 | 5.97 | 3.15 | ∞ | 1.787 | 1.148 | - |
| 80 | 0.339 | 0.592 | 0.351 | 0.055 | 0.246 | 0.008 | 7.16 | 3.41 | 44.88 | 1.969 | 1.226 | 3.804 |
| 85 | 0.341 | 0.609 | 0.341 | 0.053 | 0.229 | 0.018 | 7.43 | 3.66 | 19.94 | 2.006 | 1.297 | 2.993 |
| 90 | 0.394 | 0.628 | 0.333 | 0.000 | 0.210 | 0.026 | ∞ | 3.99 | 13.81 | - | 1.384 | 2.625 |
| 95 | 0.381 | 0.646 | 0.298 | 0.013 | 0.192 | 0.061 | 30.31 | 4.36 | 5.89 | 3.411 | 1.474 | 1.772 |
| 100 | 0.364 | 0.662 | 0.259 | 0.030 | 0.176 | 0.100 | 13.13 | 4.76 | 3.59 | 2.575 | 1.561 | 1.278 |
| 105 | 0.348 | 0.671 | 0.242 | 0.046 | 0.167 | 0.117 | 8.57 | 5.02 | 3.07 | 2.148 | 1.613 | 1.121 |
| 110 | 0.339 | 0.838 | 0.238 | 0.055 | 0.000 | 0.121 | 7.16 | ∞ | 2.97 | 1.969 | - | 1.088 |
| 115 | 0.337 | 0.817 | 0.329 | 0.057 | 0.021 | 0.030 | 6.91 | 39.90 | 11.97 | 1.933 | 3.686 | 2.482 |
| 120 | 0.305 | 0.786 | 0.301 | 0.089 | 0.052 | 0.058 | 4.43 | 16.12 | 6.19 | 1.488 | 2.780 | 1.823 |



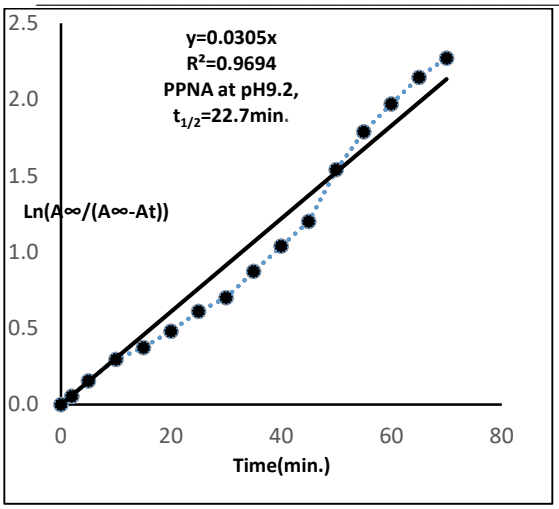



**Figure 2**
**Kinetic of complex(PPNA) absorption versus time at a temperature of (25°C), at (pH4.8, pH7.2 and pH9.2), and at the optimum wavelength for each of pH.**

Figure(2) shows that there is a direct relationship between the absorptions of the complex(PPNA) with time. It was also noticed that there was a sudden decrease in the aforementioned absorptions after (90) minutes after the formation of the drug complex at (pH4.8), after (110) minutes after the formation of the drug complex at (pH7.2), and after (75) minutes after the formation of the drug complex at (pH9.2), and then the absorption to a stable state may be due to the completion of complex formation and the termination of the reaction. And the latter does not affect the values of ($\lambda_{max}$) of the complex formed after these times, due to the end of the reaction, and this is confirmed by the values of the half-life time of its reactions, which were: (29.1min. at pH4.8), (45.3min. at pH7.2) and (22.7min. at pH9.2).

In this study, we used the integration method to follow the kinetics of complex formation reactions. When applying for the following Pseudo-first-order equation (equation(1)) to all the obtained kinetic results

And by plotting **Ln{$A_\infty$/($A_\infty$-$A_t$ )}** graph against time (in minutes), we got good straight lines at all pH functions with values ($R^2$) between (0.9694-0.997) with slopes equal to the velocity constants (k). ) Their interactions, the latter indicates that the drug complex formation reaction is of Pseudo-first-order relative to the drug. From them, the velocity constants of the complex formed at the three acidic functions and at a temperature (25°C) were calculated, which enabled us to calculate the values of its half-life times ($t_{1/2}$), which were calculated from an equation(2): (29.1min. at pH4.8), (45.3min. at pH7.2) and (22.7min. at pH9.2).

These results were identical to previous studies [17-19] on the kinetics of the reaction of the formation of Azo complexes.

From tables (2 and 3), the highest absorptions ($A_\infty$) were obtained for the formation of the two studied complexes at the three pH, their formation expiration times ($t_\infty$), their formation speed constants ($k_1$), and their half-life times ($t_{1/2}$). It is also noted from Figures (1 and 2) that an increase in the reaction rate constant of the two studied drug complexes at the three pH levels, which inevitably leads to a decrease in their half-live times. And as shown in the following table (4):

Table 4: **The values of the highest absorptions ($A_\infty$) for the formation of the two studied complexes at the three pH and $\lambda_{max}$ levels, their formation expiration times ($t_\infty$), their formation rate constants ($k_1$), and their half-life times ($t_{1/2}$).**

| No. of Complex | Symbol of Complex | pH | $\lambda_{max}$ (nm.) | $t_\infty$ (min.) | $A_\infty$ | $k_1$ (min.$^{-1}$) | ($t_{1/2}$) (min.) |
|---|---|---|---|---|---|---|---|
| 1. | PSASS | 4.8 | 433 | 100 | 0.602 | 0.0289 | 24 |
| | | 7.2 | 425 | 115 | 0.815 | 0.0172 | 40.3 |
| | | 9.2 | 419 | 90 | 0.553 | 0.0328 | 21.1 |
| 2. | PPNA | 4.8 | 439 | 90 | 0.394 | 0.0238 | 29.1 |
| | | 7.2 | 434 | 110 | 0.838 | 0.0153 | 45.3 |
| | | 9.2 | 425 | 75 | 0.359 | 0.0305 | 22.7 |

Table (4) shows the following:

1- The rate constants for the formation of the two complexes understudy in the three acid functions are of Pseudo-first-order, and the highest values for the (PSASS) complex was (0.0328 at pH9.2), and the highest values for the (PPNA) complex was (0.0305 at pH9.2). And a discrepancy was consistent with kinetic studies of different interactions in the literature ([20-30]).
2- The rate constants for the formation of the complexes ($k_1$) differ according to the reagent due to the different structures of the reagent.
3- The ($k_1$) of the two complexes differ according to the different values of the acid functions (pH).
4- The ($k_1$) of the complexes are exactly inversely proportional to their half-life times ($t_{1/2}$).
5- The wavelength of the complex ($\lambda_{max}$) changes with the change in the acid function (pH) and the change in the reagent structure forming the complex. The complex formation reaction

(PSASS) and (PPNA) take place according to the following stages[8]:

1- Converting the sulfanilic acid sodium salt or para nitro aniline to the diazotized sulfanilic acid sodium salt or diazotized para nitro aniline.
2- Coupling of the diazotized reagent with the drug understudy.

It is noticed that the azo group is coupled at the (ortho) site[31-32] relative to the phenolic group, which itself represents the (meta) site relative to the acetamide ($CH_3CONH$-) group present in the paracetamol.

**4. Conclusions**

**1-** The values of the formation rate constants of the two complexes (PSASS) and (PPNA) depend on the structure of the reagent forming each of them, as well as their difference according to the different acid functions (pH).

**2-** The values of the half-live times ($t_{1/2}$) of the formation reactions of the two complexes at the three pH levels were exactly the opposite of the rate constant values ($k_1$) for the formation of the complexes, which are shown in the previous paragraph. This indicates that the faster reaction is completed in less time.

**3-** The wavelength of the complex ($\lambda_{max}$) changes with the change in the acid function (pH) and the change in the reagent structure forming the complex.

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