



## Determination of rate constants and half-life times of complexes derived from coupling reaction 2,4-dinitroaniline and two electron-donating compounds.

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### Abstract

The research included a spectroscopic study of the kinetic reactions for the colored produced complexes derived from two different electron-donating drugs (Salicylic acid and Paracetamol) with a diazotized reagent (2,4-dinitroaniline) that accepts these electrons at different three pH functions (pH5, pH7 and pH9) and at a constant temperature (298°K).

We studied the optimal conditions for each formed complex as well as the optimal ratios (stoichiometric ratios) of its components, which were (1:10) for (drug: reagent) respectively. Then, the kinetics of the formation for the above complexes was followed spectroscopically, and it was found that these interactions was proved that drug complex formation followed a Pseudo-first-order kinetic with respect to Salicylic acid or Paracetamol drug.

We were able to calculate the rate constant( $k_1$ ) for the formation of the two produced drug compounds. The highest value( $k_1$ ) for the drug complex (SADDNA: Salicylic Acid Drug + Diazotized 2,4-Dinitroaniline) is (0.0457min<sup>-1</sup> at pH7), and for the drug complex (PDDNA: Paracetamol Drug + Diazotized 2,4-Dinitroaniline) is (0.0314 min<sup>-1</sup> at pH9). We also calculated the half-life-time( $t_{1/2}$ ) for each of them, and it was (15.17min.) and (22.08min.), respectively, which is completely opposite to the values of their rate constants under the same conditions. The reaction of salicylic acid is faster than that of paracetamol, because salicylic acid has the formula C<sub>6</sub>H<sub>4</sub>(OH)COOH, where it is an OH group ortho to a carboxyl group. That is, the carboxyl group in it obtains its resonance with the phenol ring. This is why it reacts faster compared to the acetamide group found in paracetamol.

**Keywords:** 2,4-dinitroaniline, kinetic rate-constant, pseudo-first-order kinetic, diazotized reagent, Stoichiometry, half-life-time.

### 1- Introduction

Recently, researchers have been interested in studying (donor-acceptor) complexes using absorption spectra in the Visible and Ultraviolet (UV-Visible) regions of the spectrum, because of the great importance of this type of complex, especially in the medical and biological field. In addition to the ease and accuracy of the spectroscopic method and the availability of its requirements in many laboratories, the last encouraged researchers to apply it in determining the stoichiometric ratios of different colored complexes, and then determine their stability constants, and the factors affecting on the thermodynamic parameters for them at different temperatures as well as the kinetic parameters to activate it<sup>(1-2)</sup>.

In our research we used the drugs salicylic acid and paracetamol with diazotized (2,4-dinitroaniline) reagent. And we decided to present a simplified introduction about these two drugs: Salicylic acid<sup>(3-6)</sup> is a colorless aromatic carboxylic acid that is naturally extracted from some plants such as white willow and meadowsweet. Warts and boils and useful in fighting acne is the main compound of several well-known drugs, especially aspirin. The chemical structure of salicylic acid has the formula C<sub>6</sub>H<sub>4</sub>(OH)COOH, where it is an (OH) group ortho to a carboxyl group. It is also known as 2-hydroxybenzenecarboxylic acid. It is poorly soluble in water (0.2 ml g/100 H<sub>2</sub>O at 20°C)<sup>(3-6)</sup>.

Paracetamol<sup>(7-10)</sup> 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

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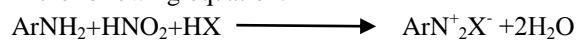
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active metabolite of phenacetin, and unlike phenacetin, paracetamol has not been shown to be carcinogenic in any way. Paracetamol does not have many side effects. It is generally used to treat fever, headache, pain and mild aches. Paracetamol is also 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<sup>(11-12)</sup>.

The diazonium salts<sup>(13-17)</sup> prepared from the reaction of amines with nitrous acid by treating sodium nitrite with a solution of amine in hydrochloric acid at (0-5°C) are important compounds in the manufacture of many organic compounds, including the azo imine complexes. As in the following equation:



In 2005 AD, the researcher Olakunle<sup>(18)</sup> and his group studied the kinetics of thermal dissociation of the ion (4-Carboxyl-2,6-dinitrobenzene diazonium) (CDNBD) by estimating the small amounts of this ion after each time period by means standard reagent as a sample for repeating two azo groups (diazo). This is in addition to estimating the rate constants for the thermal decomposition process graphically.

Another group of researchers<sup>(19)</sup> has studied the kinetics of the diazotization reactions of benzotriazole as an important organic compound in the main industrial applications. The results confirmed that the kinetic equation for the above reaction is of the first order for each of ortho-phenylene diamine and nitrous acid. The rate constant is a function of temperature.

As for our current kinetic study, it includes the kinetics of the formation of the two complexes resulting from the reaction of the two electron-

donating (salicylic acid and paracetamol drugs) with the diazotized reagent, which are (2,4-dinitroaniline) that accept these electrons, and the determination of the rate of the mentioned reaction, its rate constant (k), and the half-life time ( $t_{1/2}$ ) at the three pH functions (pH5, pH7 and pH9) with an indication of the effect of the pH function on them.

What was mentioned above is a small part of what is contained in the literature of this type of studies, and if we limit ourselves to mentioning this very brief number of these studies is due to the narrowness of the field with a certain number of research pages, and we have limited ourselves to mentioning what is recent from them, and that there are many sources It can be consulted in the literature for those interested in this type of study<sup>(20)</sup>.

## 2- Experimental part:

### 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 and 2,4-dinitroaniline. While Salicylic acid and Paracetamol drugs got from the Nineveh Drug Company (NDI).

All compounds were prepared in a standard manner similar to a previous study<sup>(15-16, 18-19)</sup>.

### 2.2- Instruments:

#### a- UV-Visible Spectrophotometers:

1-A single beam Spectrophotometer instrument manufactured by the British company (Cecil) (Cambridge, England) model (CE 1011/1000) in the range of wavelengths (325-1000nm).

2-A double beam Spectrophotometer instrument containing a computer made by the Japanese company (Shimadzu), model (UV-1800) produced in 2004 to check the value of

( $\lambda_{\text{max}}$ ) for the complexes under study 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 invisible region.

b- pH-meter : Made by (JENWAY) Company, Model (3510).

c- Water bath : Model (D3165) type (Hanigsen) manufactured by (KOTTERMANN) company.

### 2.3- Preparation of the two aqueous drug solutions of salicylic acid and paracetamol with the aqueous solution of diazotized(2,4-dinitro aniline) reagent<sup>(21-23)</sup>:

The two drugs was obtained pure in the form of a white crystalline powder from the Nineveh Drug Company, and it was used directly to prepare its two aqueous drug solutions at a concentration of ( $10^{-3}$ M), to be subsequently reacted with the aqueous solution of diazotized reagent (2,4-dinitro aniline) at a concentration of ( $10^{-3}$ M).

### 2.4- Basic solution of $\text{Na}_2\text{CO}_3$ <sup>(15-16, 18-19)</sup>:

(0.1M) of  $\text{Na}_2\text{CO}_3$  Solutions were prepared from sodium carbonate as a base solution by standard methods, and these solutions were used to control the acidic function of the drug complexes at the required values (pH5, pH7 and pH9). Experimentally, different volumes of sodium carbonate solution were added to the reagent and two drug solutions until the required acidity(pH) was obtained, because it was expected that a portion of the carbonate salt ( $\text{Na}_2\text{CO}_3$ ) would convert to carbonic acid due to the presence of hydrochloric acid (HCl) with the reagents solution. Thus, a mixture of weak carbonic acid and its salt is created, which acts as a buffer solution to adjust the pH.

### 2.5- Preparation of two drug complexes solutions<sup>(24-26)</sup>:

The aqueous solutions of the two salicylic acid and 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 ( $\text{Na}_2\text{CO}_3$ ) with (0.2ml) from ( $10^{-3}$ M) from the drug solution at a temperature of ( $298^\circ\text{K}$ ) to obtain the required acidic functions : (pH5, pH7 and pH9).

**Table(1): Numbers, symbols, and names for the two produced drug complexes.**

No. of Produced Drug Complexes	Symbol of Produced Drug Complexes	Name of Produced Drug Complexes
1	SADDNA	Salicylic Acid+diazotized(2,4-dinitroaniline) reagent.
2	PDDNA	Paracetamol+diazotized(2,4-dinitroaniline) reagent.

**Table(2): The final optimum conditions for the two prepared drug complexes are under study at a temperature of ( $298^\circ\text{K}$ ) and at (pH5, pH7 and pH9).**

Symbol of Produced Drug complexes	Optimum Order of Addition		Optimum Wavelength (nm.)
SADDNA	pH5	0.2ml( $10^{-3}$ M Salicylic Acid)+ 2.0ml( $10^{-3}$ M Diazotized(2,4-dinitroaniline)Reagent)+ 0.2ml(0.1M Sodium Carbonate).	411
	pH7	0.2ml( $10^{-3}$ M Salicylic Acid)+ 2.0ml( $10^{-3}$ M Diazotized(2,4-dinitroaniline)Reagent)+ 0.35ml(0.1M Sodium Carbonate).	407
	pH9	0.2ml( $10^{-3}$ M Salicylic Acid)+ 2.0ml( $10^{-3}$ M Diazotized(2,4-dinitroaniline)Reagent)+ 0.5 ml(0.1M Sodium Carbonate).	400
PDDNA	pH5	0.2ml( $10^{-3}$ M Paracetamol)+ 0.15ml(0.1M Sodium Carbonate)+ 2.0ml( $10^{-3}$ M Diazotized(2,4-dinitroaniline)Reagent).	444
	pH7	2.0ml( $10^{-3}$ M Diazotized(2,4-dinitroaniline)Reagent)+ 0.25ml(0.1M Sodium Carbonate)+ 0.2ml( $10^{-3}$ M Paracetamol).	438
	pH9	0.4ml(0.1M Sodium Carbonate)+ 0.2ml( $10^{-3}$ M Paracetamol)+ 2.0ml( $10^{-3}$ M Diazotized(2,4-dinitroaniline)Reagent).	429

### 2.6- Kinetic study:

The mixture of the solutions mentioned above was fixed each time at the selected temperature ( $298^\circ\text{K}$ ). As the aqueous solutions of the two drug complexes were prepared according to the optimum order of addition, as shown in Table (2).

The absorbance of each kinetic complex was followed at its optimum wavelength and until the end of the reaction or reaching its maximum value ( $\lambda_{\text{max}}$ ). The kinetic equation was applied for the 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:

The researcher relied on the best optimal conditions for the formation of the two complexes derived from the interaction of the salicylic acid drug and paracetamol drug once with the diazotized (2,4-dinitroaniline) reagent that included: the best primitive wavelength, the optimum volume of the reagent, the optimum concentration of the base, the optimum order of addition, Hence, the final optimum wavelength ( $\lambda_{\max}$ ) of the complex under optimal conditions, as mentioned in our previous studies<sup>(18-21)</sup>. In it, we confirmed that the UV and visible spectrum of the two complexes as shown in Table(1) showed spectral bands at the value of ( $\lambda_{\max}$ ), and as shown in Table(2).

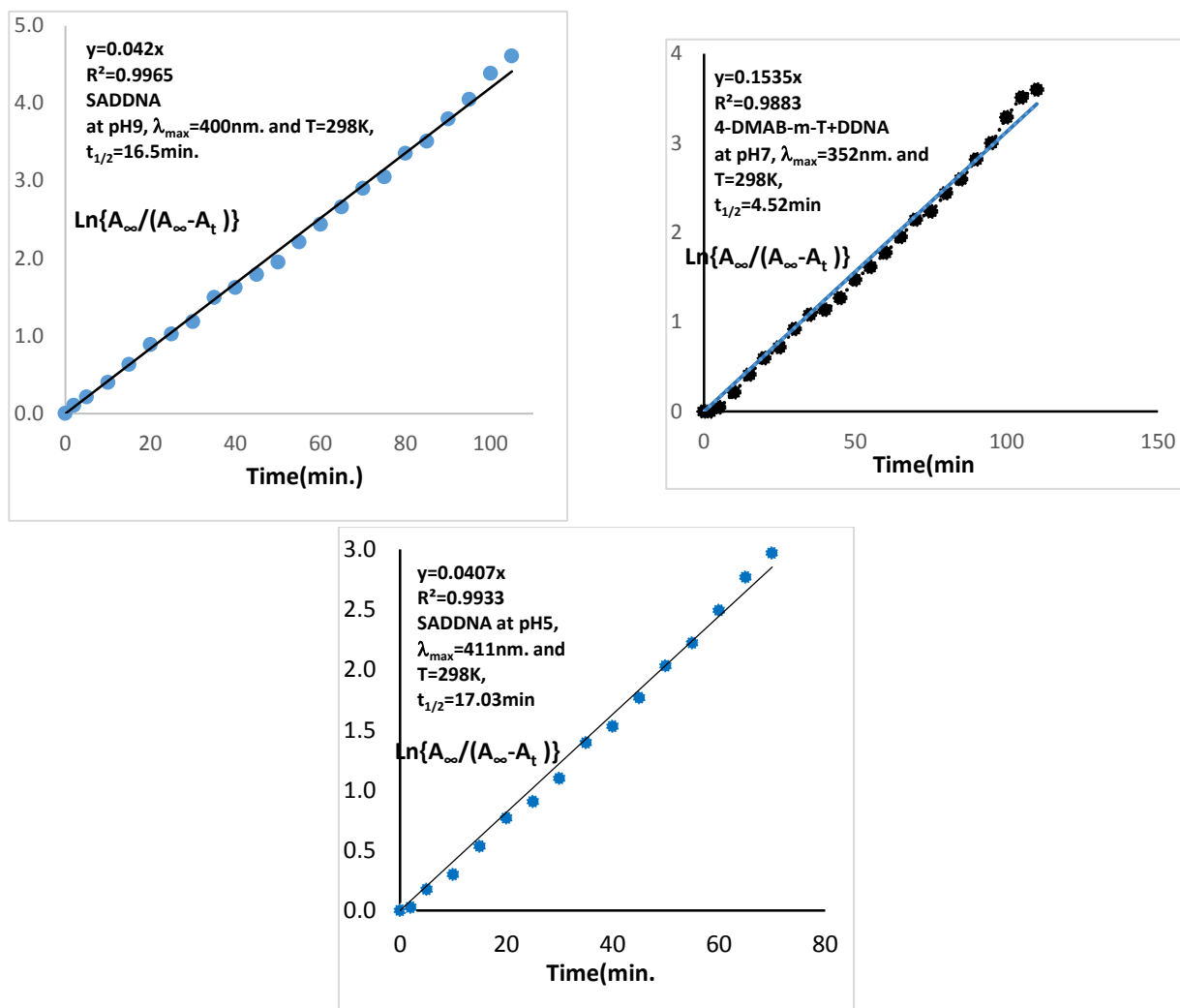
These results confirm that there are no spectral interference between the resulting complex and the reactants. Accordingly, this kinetic spectroscopy study was based on the kinematic equation model of the first order in following up the formation of the

formed drug complex, by following up the absorption of the resulting complex to a time exceeding (120) minutes. And as shown in Table (3) and Figure (1).

Figure (1) shows that there is a direct relationship between the absorbances of the complex (SADDNA) with time. It was also noticed that there was a sudden increase in the aforementioned absorbances after (75) minutes after the formation of the drug complex at (pH5), after (85) minutes after the formation of the drug complex at (pH7), and after (110) minutes after the formation of the drug complex at (pH9), 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: (17.03min. at pH5), (15.17min. at pH7), (16.50min. at pH9).

**Table (3): Monitoring produced drug complex absorbance (SADDNA) versus time at a temperature of (298 K), at (pH5, pH7 and pH9), and at the optimum wavelength for each of pH.**

Time (min)	Absorbance			$A_{\infty}-A_t$			$A_{\infty}/(A_{\infty}-A_t)$			$\ln \{A_{\infty}/(A_{\infty}-A_t)\}$		
	pH5, $\lambda_{\max}=411\text{nm}$ .	pH7, $\lambda_{\max}=407\text{nm}$ .	pH9, $\lambda_{\max}=400\text{nm}$ .	pH5	pH7	pH9	pH5	pH7	pH9	pH5	pH7	pH9
0	0.000	0.000	0.000	0.351	0.376	0.401	1.00	1.00	1.00	0.000	0.000	0.000
2	0.009	0.017	0.039	0.342	0.359	0.362	1.03	1.05	1.11	0.026	0.046	0.102
5	0.057	0.062	0.077	0.294	0.314	0.324	1.19	1.20	1.24	0.177	0.180	0.213
10	0.091	0.118	0.132	0.260	0.258	0.269	1.35	1.46	1.49	0.300	0.377	0.399
15	0.145	0.166	0.188	0.206	0.210	0.213	1.70	1.79	1.88	0.533	0.582	0.633
20	0.188	0.208	0.236	0.163	0.168	0.165	2.15	2.24	2.43	0.767	0.806	0.888
25	0.209	0.238	0.257	0.142	0.138	0.144	2.47	2.72	2.78	0.905	1.002	1.024
30	0.234	0.269	0.278	0.117	0.107	0.123	3.00	3.51	3.26	1.099	1.257	1.182
35	0.264	0.294	0.311	0.087	0.082	0.090	4.03	4.59	4.46	1.395	1.523	1.494
40	0.275	0.313	0.322	0.076	0.063	0.079	4.62	5.97	5.08	1.530	1.786	1.625
45	0.291	0.324	0.334	0.060	0.052	0.067	5.85	7.23	5.99	1.766	1.978	1.789
50	0.305	0.337	0.344	0.046	0.039	0.057	7.63	9.64	7.04	2.032	2.266	1.951
55	0.313	0.344	0.357	0.038	0.032	0.044	9.24	11.75	9.11	2.223	2.464	2.210
60	0.322	0.352	0.366	0.029	0.024	0.035	12.10	15.67	11.46	2.493	2.752	2.439
65	0.329	0.358	0.373	0.022	0.018	0.028	15.95	20.89	14.32	2.770	3.039	2.662
70	0.333	0.361	0.379	0.018	0.015	0.022	19.50	25.07	18.23	2.970	3.222	2.903
75	0.351	0.364	0.382	0.000	0.012	0.019	$\infty$	31.33	21.11	-	3.445	3.050
80	0.337	0.368	0.387	0.014	0.008	0.014	25.07	47.00	28.64	3.222	3.850	3.355
85	0.334	0.376	0.389	0.017	0.000	0.012	20.65	$\infty$	33.42	3.028	-	3.509
90	0.325	0.361	0.392	0.026	0.015	0.009	13.50	25.07	44.56	2.603	3.222	3.797
95	0.316	0.352	0.394	0.035	0.024	0.007	10.03	15.67	57.29	2.305	2.752	4.048
100	0.307	0.339	0.396	0.044	0.037	0.005	7.98	10.16	80.20	2.077	2.319	4.385
105	0.301	0.321	0.397	0.050	0.055	0.004	7.02	6.84	100.25	1.949	1.922	4.608
110	0.298	0.313	0.401	0.053	0.063	0.000	6.62	5.97	$\infty$	1.890	1.786	-
115	0.281	0.299	0.391	0.070	0.077	0.010	5.01	4.88	40.10	1.612	1.586	3.691
120	0.265	0.274	0.374	0.086	0.102	0.027	4.08	3.69	14.85	1.406	1.305	2.698



**Figure (1): Kinetic of produced drug complex absorbance (SADDNA) versus time at a temperature of (298 K), at (pH5, pH7 and pH9), and at the optimum wavelength for each of pH.**

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

$$\ln\{A_{\infty}/(A_{\infty}-A_t)\} = k_1.t \text{ -----(1)}$$

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 (0.9933-0.9965) with slopes equal to the velocity constants ( $k$ ). Their interactions, the latter indicates that the drug complex formation reaction is of the first 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 (298 K) were calculated, which enabled us to calculate the values of its half-life-times ( $t_{1/2}$ ), which were calculated

from the following second equation: (17.03min. at pH5), (15.17min. at pH7), (16.50min. at pH9).

$$t_{1/2} = \ln 2 / k_1 \text{ -----(2)}$$

These results were identical to previous studies<sup>(27-28)</sup> on the kinetics of the reaction of the formation of Azo complexes.

Figure (2) shows that there is a direct relationship between the absorbances of the complex (PDDNA) with time. It was also noticed that there was a sudden increase in the aforementioned absorbances after (100) minutes after the formation of the drug complex at (pH5), after (105) minutes after the formation of the drug complex at (pH7), and after (115) minutes after the formation of the drug complex at (pH9), and then the absorption to a stable state may be due to the completion of complex formation and the termination of the reaction.

Time (min)	Absorbance			$A_{\infty}-A_t$			$A_{\infty}/(A_{\infty}-A_t)$			$\ln \{A_{\infty}/(A_{\infty}-A_t)\}$		
	pH5, $\lambda_{\max}=444\text{nm}$	pH7, $\lambda_{\max}=438\text{ nm}$	pH9, $\lambda_{\max}=429\text{ nm}$	pH5	pH7	pH9	pH5	pH7	pH9	pH5	pH7	pH9
0	0.000	0.000	0.000	0.422	0.414	0.457	1.00	1.00	1.00	0.000	0.000	0.000
2	0.018	0.022	0.042	0.404	0.392	0.415	1.04	1.06	1.10	0.044	0.055	0.096
5	0.052	0.048	0.079	0.370	0.366	0.378	1.14	1.13	1.21	0.132	0.123	0.190
10	0.093	0.084	0.134	0.329	0.330	0.323	1.28	1.25	1.41	0.249	0.227	0.347
15	0.141	0.171	0.189	0.281	0.243	0.268	1.50	1.70	1.71	0.407	0.533	0.534
20	0.181	0.205	0.239	0.241	0.209	0.218	1.75	1.98	2.10	0.560	0.684	0.740
25	0.219	0.209	0.259	0.203	0.205	0.198	2.08	2.02	2.31	0.732	0.703	0.836
30	0.235	0.231	0.281	0.187	0.183	0.176	2.26	2.26	2.60	0.814	0.816	0.954
35	0.248	0.255	0.314	0.174	0.159	0.143	2.43	2.60	3.20	0.886	0.957	1.162
40	0.275	0.273	0.325	0.147	0.141	0.132	2.87	2.94	3.46	1.055	1.077	1.242
45	0.301	0.297	0.336	0.121	0.117	0.121	3.49	3.54	3.78	1.249	1.264	1.329
50	0.311	0.309	0.347	0.111	0.105	0.110	3.80	3.94	4.15	1.335	1.372	1.424
55	0.319	0.321	0.359	0.103	0.093	0.098	4.10	4.45	4.66	1.410	1.493	1.540
60	0.333	0.331	0.368	0.089	0.083	0.089	4.74	4.99	5.13	1.556	1.607	1.636
65	0.339	0.337	0.379	0.083	0.077	0.078	5.08	5.38	5.86	1.626	1.682	1.768
70	0.354	0.351	0.395	0.068	0.063	0.062	6.21	6.57	7.37	1.825	1.883	1.998
75	0.364	0.359	0.405	0.058	0.055	0.052	7.28	7.53	8.79	1.985	2.019	2.173
80	0.377	0.366	0.414	0.045	0.048	0.043	9.38	8.63	10.63	2.238	2.155	2.363
85	0.385	0.371	0.422	0.037	0.043	0.035	11.41	9.63	13.06	2.434	2.265	2.569
90	0.392	0.379	0.429	0.030	0.035	0.028	14.07	11.83	16.32	2.644	2.471	2.792
95	0.399	0.385	0.434	0.023	0.029	0.023	18.35	14.28	19.87	2.910	2.659	2.989
100	0.422	0.389	0.439	0.000	0.025	0.018	$\infty$	16.56	25.39	-	2.807	3.234
105	0.401	0.414	0.445	0.021	0.000	0.012	20.10	$\infty$	38.08	3.000	-	3.640
110	0.385	0.404	0.448	0.037	0.010	0.009	11.41	41.40	50.78	2.434	3.723	3.927
115	0.362	0.391	0.457	0.060	0.023	0.000	7.03	18.00	$\infty$	1.951	2.890	-
120	0.341	0.372	0.366	0.081	0.042	0.091	5.21	9.86	5.02	1.651	2.288	1.614

Table (4): Monitoring produced drug complex absorbance (PDDNA) versus time at a temperature of (298° K), at (pH5, pH7 and pH9), and at the optimum wavelength for each of pH.

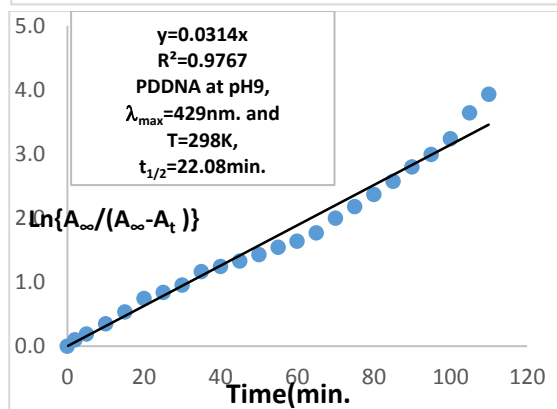
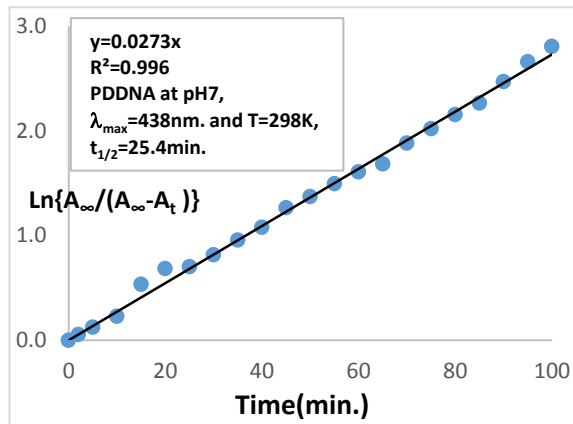
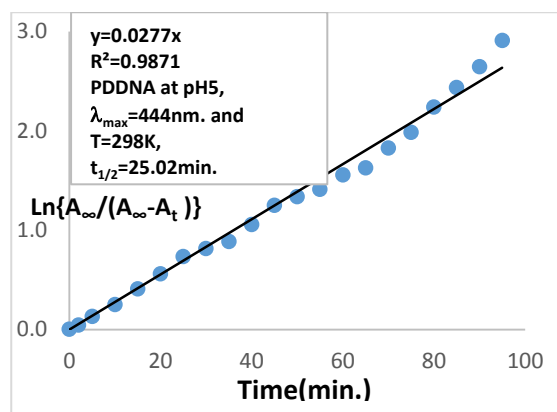


Figure (2): Kinetic of produced drug complex absorbance (PDDNA) versus time at a temperature of (298° K), at (pH5, pH7 and pH9), and at the optimum wavelength for each of pH.

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: (25.02min. at pH5), (25.40min. at pH7), (22.08min. at pH9).

In this study, we used the integration method to follow the kinetics of complex formation reactions. When applying 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 (0.9900-0.9956) with slopes equal to the velocity constants (k). Their interactions, the latter indicates that the drug complex formation reaction is of the first 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 (298°K) were calculated, which enabled us to calculate the values of its half-life times ( $t_{1/2}$ ), which were calculated from equation(2): (25.02min. at pH5), (25.40min. at pH7), (22.08min. at pH9).

These results were identical to previous studies<sup>(20-21)</sup> on the kinetics of the reaction of the formation of Azo complexes.

From tables (3 and 4), the highest absorbances ( $A_{\infty}$ ) were obtained for the formation of the two studied complexes at the three pH, their formation expiration times ( $t_{\infty}$ ), their formation rate 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-life times. And as shown in the following table (5):

Table (5) shows the following:

- 1- The rate constants for the formation of the two drug complexes under study in the three acid functions are of the pseudo-first order, and the highest values for the (SADDNA) complex were (0.0457 at pH7), and the highest values for the (PDDNA) complex were (0.0314 at pH9). And this discrepancy was consistent with kinetic studies of different interactions in the literature<sup>(20-21)</sup>.

**Table(5): The values of the highest absorbances ( $A_{\infty}$ ) for the formation of the two studied produced drug 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 Drug Complex	Symb ol of Drug Comp lex	p H	$\lambda_{\max}$ (nm. )	$t_{\infty}$ (min.)	$A_{\infty}$	$k_1$ (min <sup>-1</sup> )	( $t_{1/2}$ ) (min .)
1.	SAD DNA	5	411	75	0.351	0.0407	17.03
		7	407	85	0.376	0.0457	15.17
		9	400	110	0.401	0.0420	16.50
2.	PDD NA	5	444	100	0.422	0.0277	25.02
		7	438	105	0.414	0.0273	25.40
		9	429	115	0.457	0.0314	22.08

- 2- The rate constants for the formation of the produced complexes ( $k_1$ ) differ according to the drug due to the different structure of the drug.
- 3- The ( $k_1$ ) of the two produced drug complexes differ according to the different values of the acid functions (pH).
- 4- The ( $k_1$ ) of the produced drug 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 drug structure forming the produced drug complex.

All the above paragraphs are identical and compatible with previous kinetic studies<sup>(29-30)</sup>.

#### 4- CONCLUSIONS

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

- 2) The values of the half-life times ( $t_{1/2}$ ) of the formation reactions of the two drug complexes at the three pH levels were exactly the opposite of the rate constant values ( $k_1$ ) for the formation of the produced complexes, which are shown in the previous paragraph. This indicates that the faster reaction is completed in less time.
- 3) The wavelength of the produced complex ( $\lambda_{\max}$ ) changes with the change in the acid function (pH) and the change in the drug structure forming the produced complex.
- 4) The reaction of salicylic acid is faster than that of paracetamol, because salicylic acid has the formula  $C_6H_4(OH)COOH$ , where it is an OH group ortho to a carboxyl group. That is, the carboxyl group in it obtains its resonance with the phenol ring. This is why it reacts faster compared to the acetamide group found in paracetamol.

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