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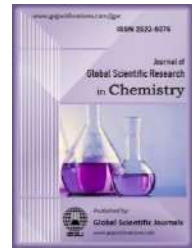

Finding the Stability Constants for the Colored Compounds Resulting from The Reaction of Five Food Dyes with the Diazotized Para-Nitro Aniline Reagent at their Natural pH

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ABSTRACT

The main subject of the study is the determination of the stability constants of these colored Azodyes formed using the spectrophotometric analysis method. As this study required steps, including: finding the optimal conditions for each colored produced Azodye, which are: the optimum wavelength, the optimum volume of the reagent, the order of addition, the stability time of the resulting complex, and the final optimum wavelength at the final optimal conditions. The second step was: Determining the stoichiometric ratios of the components of each resulting complex using the mole-ratio method, which was (1:1) for all of them. The values of the stability constants for the formed Azo complexes were calculated and found to depend on two factors: The first is the temperature: the temperature was studied within the range (273-313oK), which made it easy to calculate the thermodynamic parameters (ΔGo, ΔH, and ΔSo). , where it was found that they are spontaneous and exothermic reactions through the negative values (ΔGo) and (ΔH), respectively. The same study also showed the negative sign of entropy (ΔSo), which agrees with theoretical studies. The second factor is the structural formulas: the study proved that changing the structures of the food dyes has a clear effect on the stability constants of the resulting Azodyes.

1. Introduction

Dyes are colored ionic aromatic organic compounds resulting from chemical formation. Their electrons are not positioned, they contain different functional groups, and they contain aromatic rings in their structure.

The presence of unsaturated groups within the dye molecule plays a key role in the appearance of its color, and this explains the appearance of saturated organic compounds, and that the presence of chromophore groups is what makes the compound colored and we mean the color-bearing groups that represent the Azo group, nitro, nitrous, carbonyl, and thiocarbonyl , and ethylene. Some of these groups are highly effective in color formation (such as nitro, nitrous, and azo) in addition to the quinidide group, which is the reason for the coloring of the aromatic rings.

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As for the other part, it has a weak reactivity, such as (carbonyl), as well as the carbon double bond. In order to strengthen the color, there must be two or more groups of color-bearing groups, or they must exist in conjunction with each other or with other groups. It has also been noted that the auxiliary groups are called (oxochromates), which work to strengthen the color and increase its intensity, and they are usually electron-motive groups such as (OR, OH, NH2, NRH, NR2) in addition to the increase in the acidic and basic properties of the formula[1-6].

Colored materials are mainly divided into: Dyes and Pigments[7-20]. Pigments are materials with a special crystalline shape and known chemical composition, and they retain their crystalline and molecular structure during the process of use, and this term is given to pigments that lose their structural qualities during the process of use, and for this reason they are used in coating surfaces, inks and cosmetics. While Dyes is mainly used for dyeing different types of fibers such as cotton, wool, polyester and others[7-20].

While Azodyes are distinguished by containing the chromophore group, and they constitute more than half of the dyes used at the present time, and they vary in their complexity according to the number of azo groups and the number and nature of the oxochromic groups present in them due to the possibility of preparing different types of them and the way they are used and possessing various properties for the simplicity of their preparation methods. Therefore, it is one of the most important types of dyes at all[3-10].

Azodyes are classified according to the oxochromic groups present in them according to the international system into the following: 1- Basic if they contain a group (NR, NR, NH2). 2- Acidic if it contains a group (OH, SO3H, COOH). 3- Acidic-Basic: If it contains both groups, then it will depend on the strength and number of the linked group[1-5]..

The aromatic Azodyes also depend on the type of the ring constituting them, and they can be classified into: Homocyclic: This type of Azodyes is the least widespread and important, as its effectiveness is limited due to the absence of binding sites except for the bonding through the hydrogen atom of the Azo group with the attacking groups, Its rings may be homogeneous placed with one or more acidic and basic groups[21-30].

While heterocyclic Azodyes: This type of Azodyes is used recently as reagents in chemical analyzes, due to the presence of heterogeneous aromatic rings located on both ends of the Azo group or on one end with the presence of an atom and the importance of electrons such as[3-9]..

Azodyes are also classified into: mono-azo: which contain only one group of azo groups, or di-azo groups: this type contains two groups of azo linked by homogeneous rings or heterocyclic rings, or tri-azo: this type contains (3) groups Bridgeous linked to each other by different aromatic rings and also contains groups of different types (acidic or basic), or multi-azo: this type is characterized by the presence of (4) or more groups of azo group and consists of direct association of pigments with other pigments[7-12].

Food colorings[7-20].: Colors are considered artificial dyes or ingredients of nature for foods. Extracts derived from natural sources as containing selectively pigmented pigments for aromatic food ingredients have also been defined as food colorings. Substances that are considered food such as concentrates of fruits and vegetables and saffron used because of their coloring properties are known as food coloring and do not fall into a wide range of food additives list.

So the food industry uses natural colors or artificial dyes to make processed foods more attractive to consumers and add color to compensate for color loss due to processing or storage and to balance the difference in natural color. Color is also added to products that have no color at all, such as sugar-based candy and soft drinks, to make them attractive to consumers[7-20].

2. Experimental part

The scientific aspect is very important and essential for all applied sciences because it is very accurate in its steps and gives accurate and excellent results. This study depends largely and widely on the practical side as well as the methods of preparing chemicals and laboratory devices used.

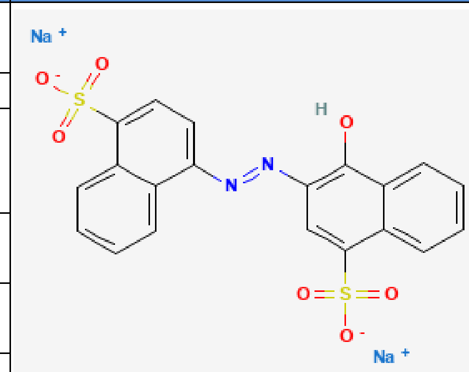
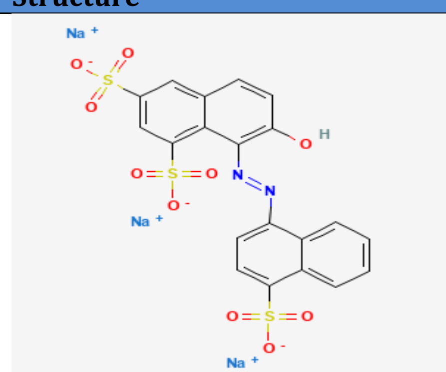
2.1- Chemicals:

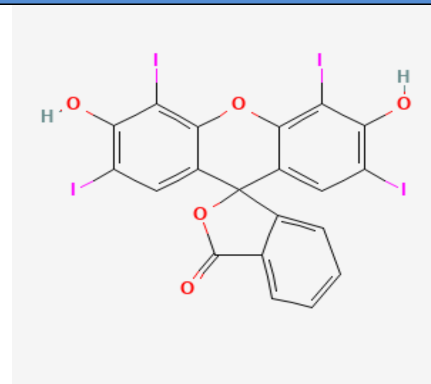
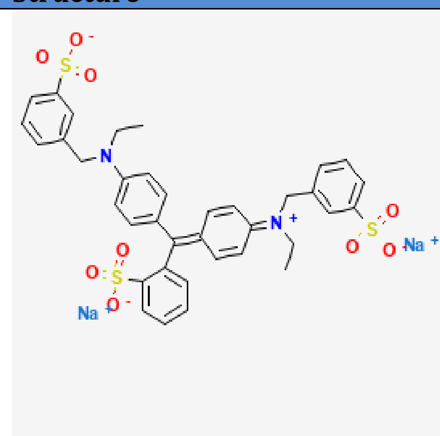
The primary chemicals as well as the solvents used in this study were supplied by my company (Fluka, BDH), and these materials are: Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Distilled water, p-Nitro aniline and Absolute ethanol.

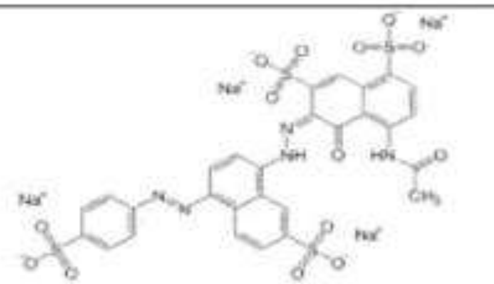
As for the studied industrial food dyes or colorings, they were supplied from the local markets in the city of Mosul, packed in sealed bottles, and from well-known international companies (industries-India) (A Jana chemical).

The following table shows the studied artificial food dyes or colors.

Table (1): names, molecular formulas and some physical properties of the studied industrial food coloring pigments[7-20].

Dye symbol	**E122**	**Structure**
Chemical family	**Mono azo**	
Trade Name	Carmoisine	
The scientific name	disodium;4-hydroxy-3-[(4-sulfonatonaphthalen-1-yl) diazenyl] naphthalene-1-sulfonate	
Chemical formula	C20H12N2Na2O7S2	
Molecular weight(g/mole)	502.44	
Ph	6-8	
Melting point(C°)	300	
λ_{max} (nm)	515	
ε (L/mole.cm)	17256	
Dye symbol	**E124**	**Structure**
Chemical family	**Mono azo**	
Trade Name	Ponceau 4R	
The scientific name	trisodium;7-hydroxy-8-[(4-sulfonatonaphthalen-1-yl)diazenyl] naphthalene-1,3-disulfonate	
Chemical formula	C20H11N2Na3O10S3	
Molecular weight(g/mole)	604.46	
pH	7-8	
Melting point(C°)	000	
λ_{max} (nm)	503	
ε (L/mole.cm)	19361	

Dye symbol	**E127**	**Structure**
Chemical family	Xanthene	
Trade Name	Erythrosin B	
The scientific name	3',6'-dihydroxy-2',4',5',7'-tetra iodospiro[2-benzofuran-3,9'-xanthene]-1-one	
Chemical formula	C20H6I4Na2O5	
Molecular weight(g/mole)	879.86	
pH	8-10	
Melting point(C°)	00	
λ_{max} (nm)	530	
ε (L/mole.cm)	12680	
Dye symbol	**E133**	**Structure**
Chemical family	Mono azo	
Trade Name	Brilliant Blue FCF	
The scientific name	disodium;2-[[4-[ethyl-[(3-sulfonato phenyl)methyl]amino]phenyl]-[4-[ethyl-[(3-sulfonatophenyl)methyl] azaniumylidene]cyclohexa-2,5-dien-1-ylidene]methyl]benzenesulfonate	
Chemical formula	C37H34N2Na2O9S3	
Molecular weight(g/mole)	792.84	
Ph	6-7	
Melting point(C°)	00	
λ_{max} (nm)	630	
ε (L/mole.cm)	81630	

	التركيبة الكيميائية Chemical Family) ((class)
Tetrasodium (6Z)-4-acetamido-5-oxo-6-[[7-sulfonato-4-(4-sulfonatophenyl)azo-1-naphthyl]hydrazono]naphthalene-1,7-disulfonate	الاسم الكيميائي (Chemical Name)
E- 151	الرقم العالمي (INS)
867.68 g/mol	الوزن الجزيئي (Molecular Weight)
$C_{28}H_{17}N_5Na_4O_{14}S_{42}$	الصيغة الكيميائية (Molecular Formula)
CC(=O)NC1=C2C(=C(C=C1)S(=O)(=O)[O-])C=C(C(=NNC3=C4C=C(C=CC4=C(C=C3)N=NC5=CC=C(C=C5)S(=O)(=O)[O-])S(=O)(=O)[O-])C2=O)S(=O)(=O)[O-].[Na+].[Na+].[Na+].[Na+]	SMILE

2.2-pH-meter:

The device used (JEN way 3510) was adjusted and calibrated using buffer solutions, and the pH function of the industrial food coloring was measured at the optimum conditions for each dye.

2.3- Preparation of solutions (10^{-3}M) for industrial food coloring dyes[7-20]:

The standard solutions of the studied industrial food colorings (E127, E151, E133, E122 and E124) were prepared by dissolving the appropriate weight of each of these five dyes in distilled water in a volumetric bottle of (100ml)and supplemented with distilled water to the mark to obtain solutions with a concentration of (10^{-3}M) ready to work and determine its stability constants and the factors affecting them[7-20].

2.4- UV-Visible Spectrophotometer:

In our study, we used a device of the type (Ta2 + UV-Vis. Spectrophotometric PG Lin) in order to find the values of (λ_{max}) for all industrial food coloring dyes and then measure the absorption spectrum of the dyes using a device (CEcil Spectrophotometric 1000S) using distilled water as a solvent and cells thick (1 cm).

2.5- Prepare a solution of (0.1M) sodium carbonate (Na_2CO_3) [21-33]:

We put (6g) of sodium carbonate on the watch bottle in an electric oven at a temperature of (110-140ºC) and dry the material well and then cool it to laboratory temperature by placing it in a desiccator for at least half an hour and then weighing (5.3g) of the dry substance. We transfer it to a beaker and dissolve it with a small amount of distilled water, then transfer it to a volumetric bottle of (500ml) and complete the volume to the mark with distilled water to obtain a standard solution of sodium carbonate with a concentration of (0.1M) to be used in the subsequent study.

2.6- Preparation of the diazotized paranitroaniline solution[21-33]:

0.1727 g) of Paranitroaniline is weighed and dissolved in (50 ml) of distilled water, then (20 ml) of (1 M) of HCl is added to it and the solution is heated to dissolve, then the mixture is transferred to a volumetric bottle (250 ml) and then cooled to temperature (0-5 °C) in an ice bath, then a solution (8.65 ml) of 1% of ($NaNO_2$) is added, then stirred for (5) minutes, then the solution is supplemented with cold distilled water to the mark, then the solution is dark placed in a vial and remains stable for a whole day after being placed in the refrigerator.

3. Results and Discussion

The development in scientific research in all areas of life, including chemistry, led to an in-depth study and preparation of many types of complexes of great importance in medical, industrial and biological terms, known as (donor-accepter) complexes, depending on spectroscopic techniques such as (U.V. and Vis. spectrophotometer).

This research includes the determination and study of the stability constants of Azodyes complexes prepared from the reaction of five food dyes with diazotized para-nitro aniline (PNA) reagent, and then finding the optimal conditions for them and the factors that affect the stability constants[33] and then find the ratios of the components (stoichiometric ratio) of the complex[34] and it appeared in our study that the stoichiometric ratio of all complex are (1:1), as will be explained in the calculations.

This type of complex is prepared in a common way as mentioned in the study (Al-Niemi , Mohammad Mahmoud , 2005). There are preparatory reactions that precede the reaction of complex formation, including azotization of the reagent (PNA) and its conversion from paranitroaniline to diazotized para-nitro aniline.

After that, the coupling reaction of the denatured reagent (PNA) occurs with the prepared compounds (food dyes) by means of the Azo group[21-32].

3.1-Study of the optimum conditions[21-32] for the prepared colored complexes:

After the four complexes under study were diagnosed by several methods, including chemical and physical ones available in our laboratories. The time has come to study the optimum conditions for the formation of complexes of Azodyes after reacting the prepared food dyes with the diazotized paranitroaniline (PNA) reagent, which is fresh azotization at a temperature of (273, 283, 293, 303 and 313 ^{o}K).

The most important optimal conditions are:

1-The optimum wavelength (λ_{max}).
2-The optimum volume for the used reagent (PNA).
3-The optimum volume of (Na_2CO_3).
4-The optimum order of addition.
5-The optimum appearance time for the complexes formed was zero minutes in the complexes studied.
6-The optimum stability time for the formed complexes.
7-The optimum temperature for the formation of complexes.

The optimum conditions for each colored dye formed by the reaction of the prepared food dye with the diazotized reagent (PNA) at natural pH and temperature (283^{o}K) were studied and carefully tabulated to avoid repetition in speech, as in the following table (2):

Table (2): Wavelengths (λ_{max}) of the five food dye solutions with diazotized paranitroaniline reagent at natural pH and temperature (283°K).

No.	Abs. for Dye	$_{max}$ for Dyeλ	Symbol for Dye
1	0.342	630	E151
2	0.039	600	E127
3	0.076	570	E124
4	0.937	519	E122
5	0.160	620	E133

A study of the optimal conditions for the colored Azodyes resulting from the reaction of food dyes with the diazotized paranitroaniline reagent at the natural pH values for each of them:

1-Find the value (λmax) for the resulting colored Azodyes(21-32):

A complex solution of the colored Azodye is prepared after mixing (0.2 ml) of (10^{-3}M) each of (food dye) and diazotized paranitroaniline reagent (PNA) that is azotized with (0.2 ml) of (0.1M) of basic salt (Na_2CO_3) in a volumetric vial of (10ml) capacity, and supplemented with distilled water to the mark, then the electronic spectra of the resulting prepared Azodye solution were measured at different wavelengths in the range (325-600 nm) at a temperature (283 K°) and at the natural pH values for each of them. We found in the laboratory that the best wavelength that gives the highest absorption of the resulting colored Azodye (0.616) is (520nm). Therefore, this wavelength was fixed to complete the next experiments.

2-Effect of the optimum volume of diazotized (PNA) reagent for the resulting colored Azodyes(21-32):

Different solutions are prepared after mixing different volumes of (10^{-3}) of diazotized (PNA) reagent with fixed volumes of each of (10^{-3}) food dye (E127) and (0.1M) basic salt (sodium carbonate(Na_2CO_3)) in a volumetric vial of (10ml) capacity, and supplemented with distilled water to the mark. The electronic spectra of each solution of the resulting colored Azodye were measured against its blank solution, at a wavelength of (520nm) , the temperature (283°K) and at the natural pH values for each of them. Get the results listed in the following table:

Table(3): The effect of the size of the reagent on the absorption of the colored Azodye complex resulting from the reaction of the food dye (E127) with the diazotized (PNA) reagent at the wavelength (520nm.) and the temperature (283°K).

ml. of (10^{-3}M) (Food Dye)	ml. of (10^{-3}M) (DPNA) Reagent	ml. of (0.1M) Na_2CO_3	Absorbance
0.2	0.1	0.2	0.657
0.2	0.2	0.2	0.680
0.2	0.3	0.2	0.684
0.2	0.4	0.2	0.685
0.2	0.5	0.2	0.691
0.2	0.6	0.2	0.691
0.2	0.7	0.2	0.697
0.2	0.8	0.2	0.749
0.2	0.9	0.2	0.718
0.2	1. 0	0.2	0.687

It is clear from Table(3) that the optimum volume of the diazotized paranitroaniline reagent, which is represented by the highest absorbance value (0.749), constituting the resulting colored Azodye complex (E127+DPNA) is (0.8 ml) at the wavelength (520nm.) and the temperature (283°K).

3-Finding the optimum order of addition[21-32]:

The optimal volumes that were proven in the second paragraph above are taken for each of (Food Dye), diazotized (DPNA) reagent and base salt (Na_2CO_3) and placed in volumetric vials with a capacity of (10ml) according to six orders of addition, then diluted with distilled water to the mark limit, and then the absorbance is measured for each colored Azodye, it is formed against its blank solution, at a wavelength of (λmax=520 nm), at its natural pH values (pH8-10), and at a temperature of (283°K), as in Table (4). As this study is important to obtain a higher stability of the colored Azodye complex formed through highest absorbance values.

Table (4): The effect of the order of addition on the absorption of the Azodye complex (E127+DPNA) resulting from the reaction of the food dye (E127) with the diazotized (PNA) reagent at (520 nm.), at a natural pH (pH8-10), and at a temperature of temperature (283°K).

Natural pH	No.	Order of Addition	Absorbance
8-10	1.	0.2ml(E127)+0.2ml(Na_2CO_3)+0.8ml(DPNA)Reagent	0.348
	2.	0.2ml(E127)+0.8ml(DPNA)Reagent+0.2ml(Na_2CO_3)	0.492
	3.	0.8ml(DPNA)Reagent+0.2ml(Na_2CO_3)+0.2ml(E127)	0.589
	4.	0.8ml(DPNA)Reagent+0.2ml(E127)+0.2ml(Na_2CO_3)	0.538
	5.	0.2ml(Na_2CO_3)+0.2ml(E127)+0.8ml(DPNA)Reagent	0.302
	6.	0.2ml(Na_2CO_3)+0.8ml(DPNA)Reagent+0.2ml(E127)	0.655

It is noted from Table (4) that the best addition sequence for the resulting colored Azodye complex (E127+DPNA) shown with the highest absorbance value (0.655) at its natural pH (pH8-10), and at a temperature (283°K) is (basic salt, then Food dye (E127), then reagent (DPNA), And as follows:

0.2ml(Na_2CO_3)+0.8ml(DPNA)Reagent+0.2ml(E127).

4-Find the value (λ_{max}) for the resulting colored Azodyes at its optimal conditions[21-32]:

The best final wavelength (λmax=520nm) was studied after obtaining the practically optimal conditions for the colored Azodye complex formed by reacting the food dye (E127) with the nitrogenous (PNA) reagent, and the basic salt (Na_2CO_3) at the normal pH (pH8-10). , and at a temperature (283°K), which is represented by the highest absorption, which is (0.657). Thus, the resulting Azodye solution became ready to complete the study of the effect of time on the formation and stability of the product, and to know the proportions of the components of the resulting complex and to find and study the factors affecting its stability constants.

5-The effect of time on the stability of the produced Azodye complex (E127+DPNA)[33-37]:

After obtaining the optimal conditions for the formation of the produced Azodye complex (E127+DPNA) in practice and described in the previous paragraphs, the effect of time on the stability constants of the produced Azodye complex (E127+DPNA) resulting from the reaction of the food dye (E127) with the reagent (DPNA) at natural pH was studied at natural (pH8-10), at a temperature of (283°K), and at optimal conditions, the resulting Azodye was stable for a period of (60min). These times are sufficient for subsequent experiments. It is clear from the foregoing that the third order after the sorter in all absorption values is believed to be within the experimental errors, and therefore it cannot be relied upon. And as shown in the following table (5):

Table(5): The effect of time on the stability constants of the Azodye complex (E127+DPNA) at optimum conditions, at a natural pH (pH=8-10), and at a temperature of (283°K).

Time(min.)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
Absorbance	0.693	0.693	0.694	0.694	0.694	0.694	0.694	0.694	0.694	0.695	0.695	0.695	0.695	0.683	0.672	0.672	0.598	0.582	0.561

6-Studying the optimal conditions for colored Azodyes resulting from the interaction of the diazotized reagent (DPNA) with the rest of the food dyes under study[21-32]:

In order to avoid repetition in speech related to the optimal conditions for the formation reactions of such Azodyes, we decided to write the final optimal conditions for the reaction of the formation of any complex of an Azodye derived from any food dye with the diazotized reagent (DPNA) at the natural pH values for each of them. As shown in the following table:

Table(6): The final optimal conditions for colored Azodyes resulting from the reaction of the diazotized reagent (DPNA) with the rest of the food dyes under study at the natural pH values for each of them.

Symbol of Produced Azodyes	**Natural pH of Produced Azodyes**	**Development time**	**Stability time**	**Optimal conditions for Produced Azodyes**
E127+DPNA	8-10	0	60	0.2ml(Na_2CO_3)+0.8ml(DPNA)Reagent+0.2ml(E127)
E122+DPNA	6-8	0	50	0.2ml(Na_2CO_3)+0.6ml(DPNA)Reagent+0.2ml(E127)
E124+DPNA	7-8	0	40	0.2ml(Na_2CO_3)+0.4ml(DPNA)Reagent+0.2ml(E127)
E151+DPNA	8-10	0	50	0.2ml(Na_2CO_3)+0.6ml(DPNA)Reagent+0.2ml(E127)
E133+DPNA	6-7	0	40	0.2ml(Na_2CO_3)+0.8ml(DPNA)Reagent+0.2ml(E127)

It is clear from Table (6) that the optimal conditions for the formation of any formed Azodye complex defined by the best addition sequence depend mainly on two factors: the first is the structural form of the food dyes under study, and the second is the natural acidity function (pH) of each of them. It is also clear from the table that the stability times for the produced Azodye complexes formed from all five food dyes with the diazotized reagent (DPNA) were within the range (40-60 min.), and these times are sufficient and appropriate to conduct upcoming scientific experiments within the same study. This study was in agreement with previous studies[21-32].

3.2-Estimation of Stoichiometric Ratios of Produced Colored Azodyes Complexes[29]:

It is not sometimes possible to give correct and accurate information about the proportions of the components of the complex by elemental analysis in the complexes, because the interfacial distances between the negative and positive ions in the solid state of the complex are few compared to the liquid state. Since our study was limited to the liquid state only, we used the spectrophotometric method[1] in the calculations, which is one of the methods of instrumental analysis.

Various research studies[21-37] have confirmed that the photometric method includes three different methods, which are the mole-ratio method, Job method, and the slope-ratio method. As confirmed by research studies (references), the mole-ratio method is the most common and can be applied to different systems. It was used in estimating the stability constants of aluminum complexes: with different Schiff rules, in addition to its use in estimating cobalt complexes binary with The reagent (Byridine - 2-methyl ketoxime) was used in the study of the resulting azo complexes by reacting the reagent of the azotized sulfanilic acid salt with different oximes .Slight modifications were made to the mole-ratio method when studying the total complexes. Provided that the hydrogen ion is not released after the interaction of the metal ion with the reagent. The latter method was applied to the total complex system resulting from the interaction of (Ni+2, Co+2, Fe+2) with a reagent (2-pyridine). aldoxime). Therefore, the mole-ratio method was used to determine the proportions of the components of all the Azodye complexes formed under study, as in the following:

When we plotted the absorbance against the ratio of the volumes of the concentrations of the food dye donor to the acceptor reagent for electrons graphically we observed first that there is a direct relationship between the absorbances of the Azodye complexes formed under study against the mole-ratios of the diazotized reagent (DPNA) and at a constant temperature of (283^oK). This relationship continues until the maximum values are reached, which represent the ratios of the components of the complexes at the natural pH of each of them. Secondly, the relationship referred to above turns into an inverse, or a negative deviation is obtained. The following table shows the mole-ratios of each colored Azo complex formed at the natural pH for each of them, and at a temperature of (283^oK).

Table(7): The mole-ratios of each colored Azo complex formed at the natural pH of each of them, and at a temperature of (283^oK).

NO.	The Acceptor	The Donor	pH Natural	Mole-Ratio
1	Diazotized para-Nitro Aniline	E127	8-10	0.6
2		E122	6-8	0.8
3		E124	7-8	0.7
4		E151	8-10	0.6
5		E133	6-7	0.8

It is noted from Table (7) that the values of the mole-ratios for the five formed Azodyes under study are limited to the range (0.6-0.8), and these numbers mean that all the mole-ratios remain (1:1), and at the natural acidity functions (pH) for each formed Azodye. This is consistent with a previous study in the field of pharmaceuticals (Mahmood, 2000). It is believed that the electron-donating molecule binds with the electron-accepting molecule at the site (Azzouz & Agha, 2005: Azzouz & AL-Niemi, 2011: Azzouz & AL-Niemi, 2012) defined as (para for one of the phenolic groups and ortho for the other). That is, the aromatic ring of the eight Schiff bases does not contribute to the complex formation process even though it contains three additional phenolic groups at the ortho, meta and para sites.

3.3-Calculation of Stability Constants for Azodyes Complexes[21-37]:

Depending on the mole-ratio method mentioned in the previous paragraph, the Azodye complex (DA) formed is formed from the reaction of the five different food dyes (A) with the azotized reagent (D) in a ratio of (1:1) and as shown in the following equation:

A+D=AD……….(1)

The equation[21-37] for calculating the stability constant can be written as follows:

$$K = \frac{[DA]}{[D][A]} \quad \text{………(2)}$$

The value of the degree of Association of the produced Azodye (α) can be known from the following relationship:

$$\alpha = \frac{[E_m - E_s]}{[E_m]} \quad \text{………(3)}$$

Es = Absorption of the resulting complex solution containing stoichiometric ratios of the reagent and the compound under study.

Em = Absorption of the resulting complex solution in the presence of excess reagent, i.e. at optimal conditions.

The [C] represents the concentration of the Azodye complex formed, and the equation for the stability constant (K) can be written in the following form:

$$K = \frac{(1-\alpha)C}{[\alpha C][\alpha C]} \quad \text{.......(4)}$$

$$K = \frac{1-\alpha}{\alpha^2 C} \quad \text{..........(5)}$$

The value of (α) is calculated from Equation No. (3), and the value of (K) can be found from Equation No. (5). The stability constant of the Azodye complex formed was calculated using the following method:

A complex solution of the Azodye formed containing a ratio of (1:1) from the food dye to the reagent was prepared. Under these conditions, the complex may be formed relatively with little absorption, we find in it (Es), and after that a solution similar to the first solution is prepared, but with an excess of the reagent, i.e. At optimal conditions and based on Table (6), and in this case the stability of the resulting complex is more and with a higher absorbance in which we find (Em), provided that (Es and Em) are measured for each solution against its imaginary solution, and then equation (3) is applied to find the value (α), and then equation (5) to find the value of (K).

Then, the complexes of all five Azodyes were studied at their optimal conditions and at five different temperatures (273, 283, 293, 303 and 313), and at the natural pH values for each of them. Equations (3) and (5) were used to calculate the degree of association (α) and the stability constant (K), respectively, and were organized as in the following table (8):

Table(8): The values of the stability constants for the complexes of all five Azodyes formed at optimal conditions, at five different temperatures (273, 283, 293, 303 and 313), at the natural pH values for each of them, and at their stability times.

No.	Symbol of Produced Azodye	pH	T(K°)	Es	Em	∝	K
1	E127+DPNA	8-10	273	0.494	0.617	0.1993	100,734
			283	0.483	0.597	0.1909	110,950
			293	0.449	0.539	0.1669	149,539
			303	0.442	0.535	0.1738	136,706
			313	0.434	0.507	0.1431	206,468
2	E124+DPNA	7-8	273	0.636	0.873	0.271	49,424
			283	0.603	0.663	0.090	4555,38
			293	0.600	0.638	0.059	5132,54
			303	0.55	0.630	0.119	310,79
			313	0.458	0.599	0.2353	69,003
3	E151+DPNA	8-10	273	0.450	0.544	0.1727	138,5411
			283	0.308	0.329	0.06382	1,148,911
			293	0.305	0.334	0.0868	605,633
			303	0.284	0.294	0.0340	4,174.5
			313	0.272	0.299	0.09030	557,789
4	E122+DPNA	6-8	273	0.753	0.861	0.12543	278,107
			283	0.743	0.853	0.1289	261,897
			293	0.738	0.826	0.10653	394,638
			303	0.705	0.801	0.1198	306,362
			313	0.666	0.781	0.1472	196,654
5	E133+DPNA	6-7	273	0.278	0.398	0.30150	38,420
			283	0.158	0.370	0.5729	6,503
			293	0.284	0.355	0.2	100,000
			303	0.153	0.329	0.5349	8,125
			313	0.131	0.379	0.5304	8,343

Then the relationship was drawn between (Ln K) against the reciprocal of absolute temperatures in Kelvin units, based on the integral Vant-Hoff equation(1,5,6), which was formulated as:

Ln K = constant - ΔH/RT .... (6)

So we obtained straight lines for the complexes of Azodyes formed, all with a slope equal to (-ΔH/R), and with a correlation coefficient (R) within the range (0.9674-0.9936) at different acidic functions (pH), and as in the following table(9), which It shows the values of the thermodynamic parameters of all the Azodye complexes formed at natural pH values and at the optimal conditions for each of them, and at their stability times:

Table (9): The values of the thermodynamic parameters of all five Azodyes formed at optimal conditions, at five different temperatures (273, 283, 293, 303 and 313), at the natural pH values for each of them, and at their stability times.

No.	Symbol of Produced Azodye	pH	T(K°)	Ln K	ΔH K.J.mol-1	ΔG° K.J.mol-1	ΔS° J.mol-1.K-1	$ΔG°_{Av}$ KJ.mol-1	$ΔS°_{Av}$ KJ.mol-1
1	E127+DPNA	8-10	273	13.82281	11612.16	-31.373	157.458	-34.542	157.167
			283	13.91932		-32.750	156.757		
			293	14.2119		-34.632	157.831		
			303	14.3368		-36.116	157.520		
			313	14.5404		-37.838	157.988		
2	E124+DPNA	7-8	273	13.32604	-30315.3	-30.246	-30204.5	-30.306	-30.211
			283	12.97253		-30.522	-30207.5		
			293	12.60532		-30.706	-30210.5		
			303	11.8265		-29.792	-30217		
			313	11.63051		-30.265	-30218.6		
3	E122+DPNA	6-8	273	15.44827	-34868.1	-35.0633	-34739	-34.864	-34.748
			283	14.72041		-34.6351	-34745		
			293	14.41489		-35.1147	-34784		
			303	13.66803		-34.431	-34754		
			313	13.48029		-35.079	-34756		
4	E133+DPNA	6-7	273	11.02474	-5925.2	-25.023	113.363	-27.240	113.1925
			283	11.0827		-26.076	113.0788		
			293	11.13869		-27.133	113.0788		
			303	11.30531		-28.479	112.829		
			313	11.33176		-29.488	113.142		
5	E151+DPNA	8-10	273	11.4354	-22911.7	-31.181	30.292	-31.753	30.176
			283	11.16658		-31.691	31.022		
			293	10.59135		-31.409	29.003		
			303	10.3235		-31.806	29.357		
			313	10.2546		-32.677	31.201		

Based on Table(9), the factors affecting the values of the stability constants of the five Azodye complexes formed can be clarified, as follows:

3.4-Factors Affecting Stability Constants of Azo Complexes[21-37]:

1-Effect of Temperature and The Thermodynamic Parameters[21-37]:

The researchers found that the temperature has many effects in many chemical reactions, and in this section we will discuss the effect of temperature in the different reaction systems that contain the Azo group **(-N=N**) formed in the complexes of the Azodyes under study, due to its direct relationship to the research.

Various studies[21-37] confirmed that for temperature and thermodynamic variables clear effects in the multiple interactions of Schiff bases and oximes such as the pKa of acids and bases[21-37] and agglomeration and recently conducted research groups A thermodynamic study of the reactions of the formation of nitrogen complexes[21-37].

Based on the foregoing, the stability constants were calculated for the five Azodye complexes formed from the reactions of the five food dyes, with the diazotized reagent (DPNA). The change in the values of the stability constants of the resulting five Azodye complexes associated with temperature changes encouraged us to study these interactions thermodynamically, i.e. to extract the variables **(ΔG^o, ΔH, and ΔS^o)**, as shown in Table(9) above. Table (9) generally shows a decrease in the values of the stability constants of the Azo complex formed at a high temperature, which is proven by the increase in the degree of Association shown in Table(8). Table(9) shows the different (ΔH) values of the negative sign and the temperatures that gave stability constants. The negative sign also indicates that the reactions of forming Azo complexes are exothermic.

As for the values of (ΔG^o) for the above-mentioned reactions, they were calculated from the following well-known mathematical relationship[1]:

$\Delta G^o = - RT \ Ln \ K$ ………………………… (7)

The negative values shown in Table(9) confirm that the Azo complex formation reaction is spontaneous.

Finally, the change in reaction entropy (ΔS^o) has been calculated from the following well-known equation:

$\Delta G^o = \Delta H - T.\Delta S^o$ ……………………….(8)

The positive sign of the thermodynamic variable (ΔS^o) means that the values of S2 must be greater than S1. As for the negative sign of the variable itself, it means that the values of S1 are greater than S2, since (ΔS^o) theoretically should be negative, and this is consistent with some of the compounds studied And in different acidity functions. As for most of the compounds, they gave positive values, and this is not consistent with what was mentioned above. The reason for the positive sign of these compounds is attributed to the strength of the interfacial hydrogen bonds[1,5 and 6] formed between the reactants, i.e. Schiff bases, the diazotized reagent, and the aqueous medium, which are greater than the strength of the hydrogen bonds formed between the resulting complexes and the aforementioned solvent, and this is accompanied by a decrease in the randomness of the formation reaction systems. Azo complexes under study. Therefore, it is not surprising to obtain positive values for (ΔS^o). Finally, different values of **(ΔG^o, ΔH, and ΔS^o)** were obtained as a result of the different structures of the compounds under study. This is expected and consistent with many studies[21-37] the previous one.

2. Effect of Structural Formulas

There is no doubt that the change of structural bodies and compensators has a direct impact on many chemical reactions, as the compensators affect the stability constants of the complexes[21-37] formed from the interaction of food dyes with the reagent, as well as affect the electronic spectra of the resulting Azo complexes. When comparing the values of the stability constants of the five resulting complexes under study, we find that they differ according to the structures of the food dye constituting the complex.

4. Conclusions

1- The study proved the formation of the five Azodye complexes formed, and this was confirmed when a spectral peak appeared for each complex formed at a high wavelength compared to the Electronic spectrum (U.V+Visible) of the food dye and the diazotized reagent used, and this talk is consistent with the literature(21-37).

2- When studying the optimal conditions for the interaction of the formation of the five Azodye complexes under study, it was found that the optimal conditions depend on the structure of the electron-giving food dye molecules and the temperature of the produced solution.

3- The stability times of the five Azodye complexes under the study called the stability period were generally stable and for a limited period of time between 40 and 60. Which facilitated all physical studies related to it, such as calculating the stability constants of the resulting complexes, and the thermodynamics parameters of complexes.

4- The Mole-Raito Method for determining the proportions of the components of the five resulting Azodye complexes showed that the union ratios of the components of the resulting complex were (1:1) in all of them. This is consistent with a previous study(21-37) on other similar Azoimine complexes.

5- The effects of confined temperatures between (273-313 ^oK) were studied in the values of the stability constants of the five Azodye complexes, and showed obtaining a direct relationship linking Ln K against 1/T, and this study facilitated the extraction of thermodynamic parameters for the formation reactions of the five Azodye complexes that showed What follows:

a- The Azo reactions were all spontaneous from calculating the variable (ΔG^o) with negative sign. The reactions of the five Azodye complexes from the aforementioned inverse relationship are emitting(21-37).

b- (Exothermic reaction) by calculating the enthalpy of forming complexes (ΔH) with a negative sign, which is in agreement with the literature(21-37).

c- The change of Entropy values for Azo reactions or the formation of complexes (ΔS^o) were negative and consistent with the formation of complexes, but with the exception of some compounds that gave positive values for (ΔS^o). The latter is explained by the strength of hydrogen bonds in the reactants which are greater than the products. The negative sign (ΔS^o) is an important evidence for the formation of Azo complexes. As well as the emergence of distinct colors during preparation.

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