Chelonian Conservation And Biology

Vol. 19No.1 (2024) | https://www.acgpublishing.com/ | ISSN - 1071-8443

DOI:doi.org/10.18011/2024.01(1). 1021-1031

STUDY OF THE EFFECT OF TEMPERATURE ON THE STABILITY CONSTANT OF A NUMBER OF AZO DYES FORMED FROM A REAGENT REACTION (*O*-PHENYLENE DIAMINE) WITH SOME CHALCONES

Hiba Salah Ahmeed[1*], Ebtahag Z. Sulyman[2], Mohammad Mahmoud Hussein Al-Niemi[2]

[1*,2]Department of Chemistry, College of Education for Girls, University of Mosul, Mosul, Iraq.
[*]Email: hiba.23gep77@student.uomosul.edu.iq, [2]Email: ebthalim@uomosul.edu.iq
[3]Department of Chemistry, College of Education for Pure Science, University of Mosul, Mosul, Iraq. Email: drmohammadalhusseiny@uomosul.edu.iq

***Corresponding Author:** Hiba Salah Ahmed
*Email: hiba.23gep77@student.uomosul.edu.iq

Abstract: Our work involves a spectroscopic investigation of how pH affects the thermodynamic production of azo dyes, which are created when certain chalcones react with the isotactic reagent ortho-phenylenediamine at the dye's natural acid function at a fixed temperature (298 K). We looked at the ideal circumstances for every created azo dye along with the optimal molar ratios of its component parts, which were (2:1) for the reagent to the chalcone.

For the produced azo dyes, the stability remained constant throughout three acidic levels and six temperature ranges (273, 283, 293, 303, 313, 323 K). Then we found stability constants at the six temperatures mentioned above, It enabled us to determine that, based on the negative values of ($\Delta G°$ and ΔH), respectively, the reactions that generate azo dyes are spontaneous and heat-emitting.

Keywords: Chalconates, Azo dyes, o-phenylenediamine, Stability constants

1- Introduction:

Chalcones are one of the alpha-, beta-unsaturated ketogenic carbonyl compounds. The chalcone is (1,3-diphenyl-2-propen-1-one) and is a ketone compound containing two benzene rings with a carbonyl group linked to a double bond at the alpha and beta positions[1].

The chalcones contain substituting groups on the benzene ring at various locations (*o-, m-, p-*), and the presence of two aromatic rings on either end of the chalcone shows the tropism of the rings with the (C=C-C=O) system, which increases the effect of the substituting groups on them, whether the groups are pulling or pushing electrons[2]. The most well-known uses for diazonium salts, which are thought to be among the most significant compounds, are in the azo compound preparation process and the nitrous acid-primary amine reaction, which occurs when the amine solution is applied to sodium nitrite at a temperature of between 0 and 5°C and there is an acidic mineral present, like hydrochloric or sulfuric acid.

This mechanism is known as the nitration reaction[3].

Adel Azouz and Muhammad Al-Naimi, researchers, examined how synthetic bodies affected the stability constant values for azo dyes, which are created when imines react with the sodium salt of isozonated sulfanilic acid. The stability constants of the dyes were ascertained by the researchers by use of the photometric approach. The stability constants of the same oximatic imines in the syn- and anti-forms were then compared. as well as Schiff bases that had substituents with (CH3, NO2, NH2, OH) in them, Since sodium salt of iodinated sulfanilic acid is an electron acceptor, they also investigated the impact of temperatures in the range of (15–55) °C on the stability constant values of azo dyes generated by the interaction of salt with electron-donating imines [4,5].

We are currently investigating the best conditions, stability constants, and the effect of pH on the generation of several azo dyes from the isotactic reagent (o-phenylenediamine) reaction with chalconate at six different temperatures (0, 10, 20, 30, 40, and 50)°C and at the pH of nature.

2- Practical part:

2-1 Chemicals:

Companies Fluka (Switzerland), PRS (Spain), and BDH (England) provided the chemicals utilized in the study, which included sodium carbonate, hydrochloric acid, sodium nitrate, and o-phenylene diamine.

2-2 The devices used are:

a- Photometric spectrometer devices:

Two of the following gadgets were employed in the study: The first is a single-track instrument that measures (λmax) the organic complexes and reagents under investigation, determines the ideal circumstances, and finishes the remaining research. Model number CE 1011/1000, it is manufactured by the Cambridge, England-based British company Cecil. It operates in the wavelength range of 325–1000 nm. Regarding the second, a dual-track photometric spectrometer, the track has a computer made by the Japanese business Shimadzu, model UV-1800, which was produced in 2004. Its goal is to calculate the (λ_{max}) value of the reagents utilized or the organic compounds under investigation, as well as to draw various electronic spectra with water solvent and within the constrained range of 190-900 nm. Both devices used quartz cells from the invisible area.

b- A pH measuring device manufactured by the (JENWAY) company model (3510).

c- A water bath manufactured by the German manufacturer KOTTERMANN, model D3165, type Hanigsen.

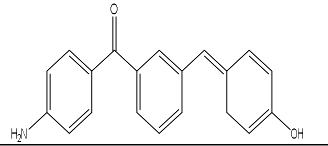
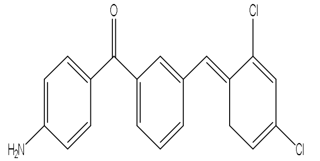
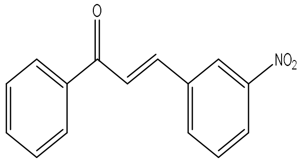
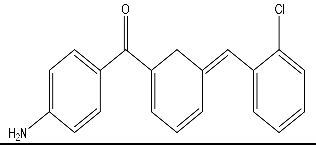
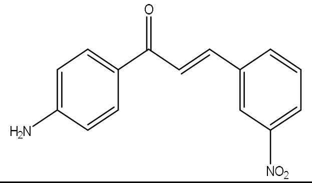
2-3 Preparation of *o*-phenylene diamine (*o*-phDA) solution:

The mixture is transferred to a volumetric flask (250 ml), After lowering the temperature to (5-0°C) in an ice bath, weigh (0.027 g) of o-phenylenediamine and mix it with (50 ml) of distilled water. Next, add (10 ml) of a 1 M solution of hydrochloric acid. Heat the solution to dissolve it. Following a few minutes of stirring and the addition of 8.65 ml of 1% NaNO2, the mixture is then transferred to the volumetric flask along with the necessary amount of cold water. Every time, the preparation is applied right away and the solution is stored in a cool, dark area.

2-4 Prepare solutions (10^{-3} M) of the five chalcones:

In a 250 ml volumetric flask, dissolve the necessary weight of each of the five compounds in ethanol. Into the mixture, add enough distilled water to obtain solutions with a 10^{-3} M concentration, which are ready to be used to make azo dyes. The names, symbols, structural formulas, and molecular weights of chalcones are shown in the following table so that their stability constants and the factors influencing them can be found and studied:

Tab. (1) structural formulae and physical characteristics of five produced compounds

Comp. No.	Symbol of 2,4-Comp. Derivatives	Nomenclature	M.Wt	Structure
1	APHCDMPM	(E)-(4-aminophenyl)(3-((4-hydroxycyclohexa-2,4-dien-1-ylidene)methyl)phenyl)methanone	303.4	
2	APDCCDMPM	(E)-(4-aminophenyl)(3-((2,4-dichlorocyclohexa-2,4-dien-1-ylidene)methyl)phenyl)methanone	356.2	
3	NP-1-PP	(E)-3-(3-nitrophenyl)-1-phenylprop-2-en-1-one	253.3	
4	APCBCDM	(Z)-(4-aminophenyl)(5-(2-chlorobenzylidene)cyclohexa-1,3-dien-1-yl)methanone	321.8	
5	APNPP	(E)-1-(4-aminophenyl)-3-(3-nitrophenyl)prop-2-en-1-one	268.3	

2-5 Preparation of solutions of aromatic azo dyes:

Table (2) lists the optimal conditions for preparing aqueous solutions of the five aromatic azo dyes. To do this, combine the required concentrations of the reagent (10^{-3} M) with the chalcone solution (10^{-3} M).

3- Results and discussion:

Because of the advancements in scientific research occurring in many spheres of life, incorporating chemistry, extensive research, and preparation of many complexes known as (donor-receiver) complexes, which are crucial to life, medicine, and industry. This work has been done using spectroscopic methods like electronic spectra. Our study first focuses on identifying the ideal circumstances for each dye's synthesis from the o-phenylene diamine reagent's coupling process, as an electron acceptor, with each of the electron-donating chalcones at six temperatures (0, 10, 20, 30, 40, 50) °C and at the natural pH. The ideal conditions for the dye components were the ideal reagent size, the ideal beginning wavelength, the ideal addition sequence, and the ideal end wavelength for dye creation and the ideal ratios for the chalcone and reagent were 2:1. This is consistent with other research [7-9], and Table (2) displays the ideal temperature (298 K) for the five aromatic azo dyes.

Tab. (2) ultimate ideal circumstances for the aromatic azo complexes produced when all of the chalcones under investigation reacted with the o-phenylene diamine reagent at 25°C and a normal pH

No.	Optimal conditions for azo dyes	λ_{max} (nm.)
APHCDMPM + o-phDA	0.5ml (ch) + 0.5ml Na_2CO_3 + 0.3ml Reagent	346
APDCCDMPM + o-phDA	0.5ml Na_2CO_3 +0.5ml (ch) + 0.3ml Reagent	335
NP-1-PP + o-phDA	0.5ml Na_2CO_3 +0.5ml (ch) + 0.3ml Reagent	334
APCBCDM + o-phDA	0.5ml Na_2CO_3 + 0.3ml Reagent + 0.5ml (ch)	340
APNPP + o-phDA	0.5ml (ch) + 0.5ml Na_2CO_3 + 0.3ml Reagent	382

3-1 Calculating the stability constants of azo dyes:

Equation No. (1) illustrates that the aromatic azo complex (DA), which is created when various chalcones (A) react with the azo reagent (D), yields a ratio of (2:1) based on the molar ratio technique.

$\rightleftharpoons$ A+D AD ……(1)

The stability constant can be calculated using the following equation [10]:

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

To calculate the degree of dye dissociation (α), using next equation:

$$\propto = \frac{[A_m - A_s]}{[A_m]} \quad \text{.........(3)}$$

As = absorbance of the resultant dye solution, which has the investigated chemical and reagent in equal amounts.

Am = absorbance of the final dye solution under ideal circumstances for the generated dye's production.

$[(1-\alpha)C]$ indicates the amount of aromatic azo dye that was generated, and for calculate the dye stability constant (K), from equation (5 and 6):

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

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

$$K = \frac{(1-\propto)}{\propto^3 - C^2} \quad \text{..........(6)}$$

Equation (3) can be employed to calculate the value of (α), and equation (5) can be utilized to ascertain the value of (K). The subsequent process was employed to ascertain the stability constant of the resulting aromatic azo dye:

Chalcone and reagent were mixed in a ratio of 2:1 to create a solution of the aromatic azo dye. We discover (As) in it because the dye absorbs comparatively little under these circumstances. Then, using Table 1 as a basis and optimal conditions, a solution akin to the first is created (1). Since the dye formed in this instance is more stable, we can find (Am) with higher absorption, but only if (As and Am) for each solution are measured against its blanck solution. Next, the value of (α) is found using equation (3), and the value of (K) is found using equation (5).

Tab. (3) The values of the aromatic azo dyes' stability constants (K) prepared at room temperature and pH under ideal circumstances for each of them, as well as within their stability periods

No.	Symbol of Prepared Dye	T (K)	A_s	A_m	α	K
1	APHCDMPM + o-phDA	273	2.015	2.612	0.23	6460980084
		283	2.951	3.921	0.25	4971044963
		293	2.655	3.611	0.26	3962286050
		303	2.665	4.012	0.34	1755158230
		313	1.962	3.469	0.43	689870931.4
		323	1.751	3.912	0.55	270473328.3
2	APDCCDMPM + o-phDA	273	1.333	1.825	0.270	3727868452
		283	1.788	2.499	0.285	3106642108
		293	1.596	2.413	0.339	1704046185
		303	1.266	2.131	0.406	888284906
		313	1.261	2.142	0.411	846108960
		323	1.082	2.241	0.517	349028319
3	NP-1-PP + o-phDA	273	1.589	1.625	0.647	130185548.7
		283	1.478	1.740	0.891	15491968.9
		293	1.277	1.661	0.892	15181293.2
		303	1.562	1.801	0.934	8144402.8

		313	1.435	1.761	0.946	6361641.6
		323	1.287	1.718	0.969	3422433.7
4	APCBCDM + o-phDA	273	1.981	2.477	0.200	9960736677.925
		283	1.863	2.459	0.242	5320973954.991
		293	1.918	2.573	0.255	4518603925.553
		303	1.922	2.657	0.277	3417232081.241
		313	1.981	2.775	0.286	3047536691.971
		323	1.794	2.916	0.385	1079987943.485
5	APNPP + o-phDA	273	2.271	2.751	0.174	15540844067
		283	2.501	3.216	0.222	7076648857
		293	2.508	3.295	0.239	5586170319
		303	1.772	2.364	0.250	4773023161
		313	1.962	2.651	0.260	4215613560
		323	1.746	2.387	0.269	3777243555

3-2 The effect of temperature and thermodynamic variables on the formation of dyes:

Numerous impacts of temperature have been verified by research studies. Because it directly relates to research, in this paragraph, We'll talk about how temperature affects a number of reaction systems that involve the azo group (-N=N-) in the investigated aromatic azo complexes. Numerous investigations have demonstrated that the influence of temperature and thermodynamic parameters was apparent in the various processes involving Schiff bases and oximes, such as agglomeration, tautomerism, and the pKa of acids and bases. Stability constants for aromatic azo dyes have been determined based on a thermodynamic investigation of the processes that generate azo complexes, which has been carried out recently by research groups. created by the interaction of the reagent o-phenylenediamine with chalconate.

The resulting azo dyes' stability constant values vary, and this fluctuation is related to temperature changes, encouraged us to study these reactions from a thermodynamic perspective, that is, to extract the ΔG^0, H, and ΔS^0 variables. The following formulation of the van't Hoff integral equation was used to calculate the thermodynamic variable (ΔH):

$$\ln K = \text{constant} - \frac{\Delta H}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

Where K : stability constant for the synthesis of the aromatic azo dye that results.

ΔH = enthalpy of the process that produces the aromatic azo dye.

The enthalpy of the reaction (ΔH) can be found using Equation No. (6). For azo dyes, we can obtain straight lines with a correlation coefficient (r) between 0.8601-0.9509 by plotting lnK against the reciprocal of the absolute temperature and at the pH Natural, as in Figures (1-5).

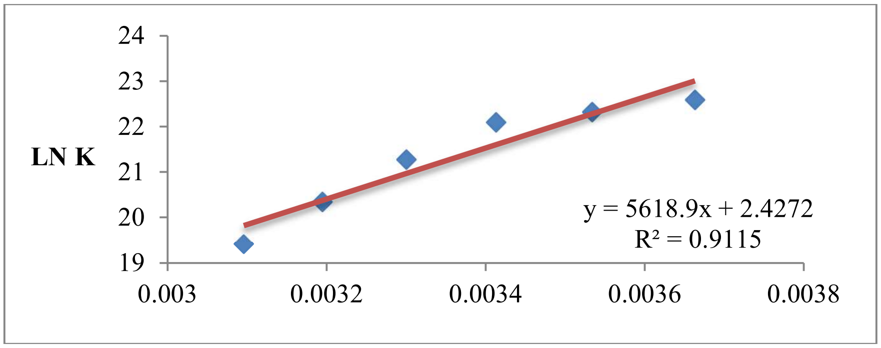


Fig. (1) Relationship between (LnK) against (T\1) for the dye APHCDMPM + o-phDA at normal pH

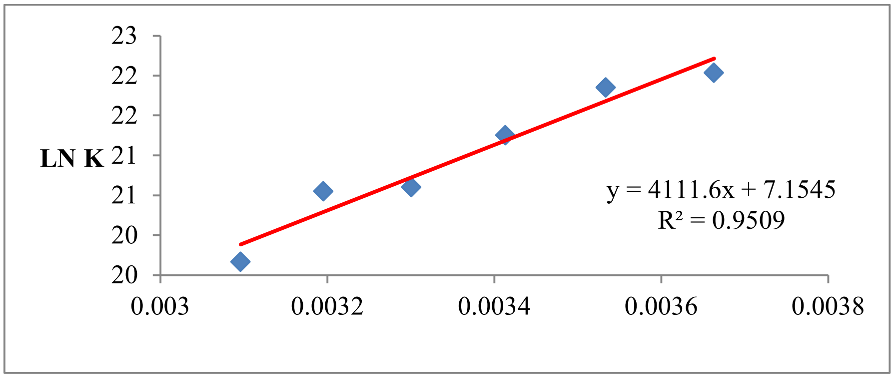


Figure (2) Graphical relationship between (LnK) against (T\1) for the dye APDCCDMPM + o-phDA At normal pH

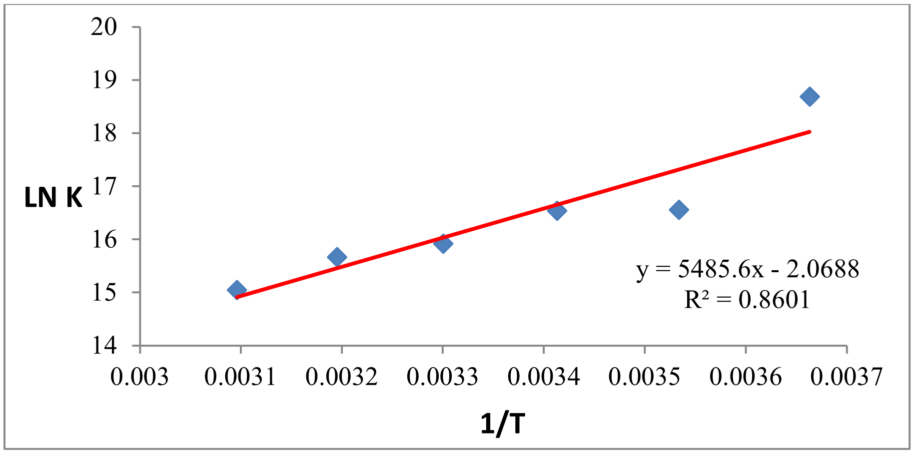


Fig. (3) Relationship between (LnK) against (T\1) for the dye NP-1-PP + o-phDA at normal pH

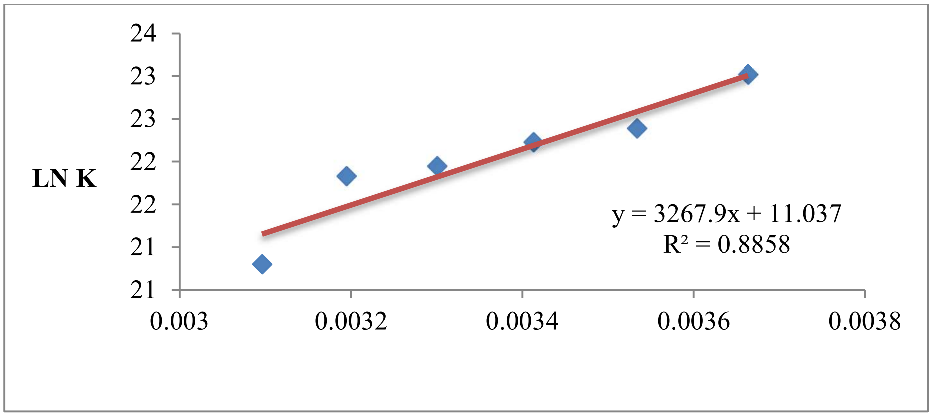


Fig. (4) Relationship between (LnK) against (T\1) for the dye APCBCDM + o-phDA at normal pH

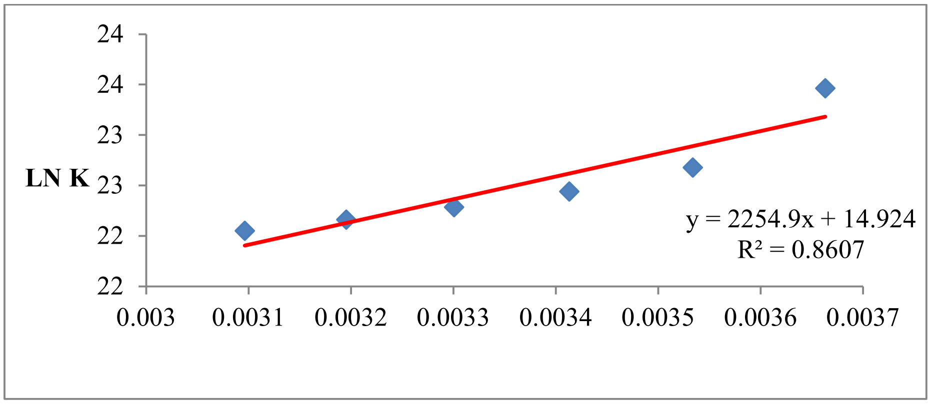


Fig. (5) Relationship between (LnK) against (T\1) for the dye APNPP + o-phDA at normal

Tab. (4): Effect of temperature and thermodynamic variables on the formation reaction of aromatic azoimine dyes at normal pH

Comp. No	Symbol of Drug-Dye	T (K)	lnK	ΔG^0 (KJ. mo1^{-1})	ΔH (KJ. mo1^{-1})	ΔS^0 (J. mo1^{-1}. K^{-1})
1	APHCDMPM + o-phDA	273	22.59	-51270.9	-46715.5	16.68616
		283	22.33	-52532.1	-46715.5	20.55325
		293	22.10	-53835.9	-46715.5	24.30144
		303	21.29	-53622	-46715.5	22.79367
		313	20.35	-52961.7	-46715.5	19.95574
		323	19.42	-52139.3	-46715.5	16.79186
2	APDCCDMPM + o-phDA	273	22.0	-50022.6	-34183.8	58.018
		283	21.9	-51426.1	-34183.8	60.927
		293	21.3	-51780.3	-34183.8	60.056
		303	20.6	-51906.4	-34183.8	58.490
		313	20.6	-53492.9	-34183.8	61.690
		323	19.7	-52824	-34183.8	57.710
3	NP-1-PP + o-phDA	273	18.7	-42408.6	-45607.3	-11.717
		283	16.6	-38953.6	-45607.3	-23.511
		293	16.5	-40280.7	-45607.3	-18.179

		303	15.9	-40086.7	-45607.3	-18.220
		313	15.7	-40766.8	-45607.3	-15.465
		323	15.0	-40404.5	-45607.3	-16.108
4	APCBCDM + o-phDA	273	23.02	-52253.4	-27169.3	91.8829
		283	22.39	-52692.2	-27169.3	90.18672
		293	22.23	-54155.9	-27169.3	92.10438
		303	21.95	-55300.4	-27169.3	92.84201
		313	21.84	-56827.6	-27169.3	94.75486
		323	20.80	-55857.4	-27169.3	88.81745
5	APNPP + o-phDA	273	23.5	-53263.0	-18747.2	126.431
		283	22.7	-53363.1	-18747.2	122.317
		293	22.4	-54672.6	-18747.2	122.612
		303	22.3	-56142.2	-18747.2	123.416
		313	22.2	-57671.9	-18747.2	124.360
		323	22.1	-59219.6	-18747.2	125.302

From Table (4), it appears in general The increase in the degree of disintegration value shown in Table (3) shows that when temperatures rise, the values of the stability constants for the azo dyes that are generated decrease. Table (4) additionally demonstrates that the various (ΔH) values have a negative sign at temperatures, which results in stability constants. The exothermic nature of azo dye formation reactions is indicated by values with a negative sign (ΔH).

(ΔG^0) for the above reactions were calculated from the following equation:

$\Delta G^0 = - RT \ln K$ ………………………… (7)

The azoimine dye formation reaction is confirmed to be (spontaneous) by the negative sign of (ΔG^0) values displayed in Table (4).

Using the following equation, the reaction's change in entropy value (ΔS^0) was determined:

$\Delta G^0 = \Delta H - T.\ \Delta S^0$ …………………………(8)

The thermodynamic variable (ΔS^0) has a negative sign, indicating that the values of S_1 are greater than S_2, which is consistent with the compounds studied having different pH values. In theory, (ΔS^0) should also have a negative sign. Contrary to what was previously stated, the positive sign of the value of (ΔS0) indicates that the values of S_2 are greater than S_1. The compounds' positive sign is caused by the strength of the hydrogen bonds that form between the reagent, chalcones, and aqueous medium during the reaction. This strength is accompanied by a decrease in the randomness of the formation reaction systems of the azo complexes under examination, and it is stronger than the hydrogen bonds that form between the produced complexes and the solvent previously indicated. Therefore, it is not surprising to discover positive values for (ΔS).

Furthermore, distinct values were acquired for ΔG^0, ΔH, and ΔS^0, due to the different compositional bodies of the dyes. This is expected and consistent with many studies[10-21].

4- Conclusions:

A - The results explained that the reaction of chalconate with the reagent produced colored azo dyes, and that the dye formed at a wavelength greater than the wavelengths of the spectra of the chalcone and the reagent alone, causing a spectral peak to appear in the electronic spectrometer.

B - It was found that the optimal molar ratio for the azo reagent and chalcone, respectively, is 2:1 for each of the azo colors generated.

C - It turns out that the values of (ΔH) are negative in sign, and indicate that the formation reactions of azo dyes are heat-emitting. Together with the positive sign of the thermodynamic variable (ΔS^0) due to the strength of the hydrogen bonds that form between the chalconate, azo reagent, and aqueous medium during the reaction, the values of (ΔG^0) are negative, confirming that the reaction to form the azo dye is spontaneous. The strength of the hydrogen bonds that form between the generated complexes and the solvent that was previously described indicates that this is followed by a decrease in the unpredictability of the formation reaction systems of the azo complexes under consideration.

D - The change in the values of the stability constants of the single dye created when its formation reaction temperature is changed indicates the effect of the reaction temperature on the stability constants. The stability constant of the resultant dye diminishes with increasing temperature; this conclusion is scientifically backed by the development of negative enthalpy values, which signify an exothermic reaction.

The aforementioned findings are all anticipated and in line with other earlier investigations [10, 12, 13, 16-21].

5- Thanks and appreciation:

References

1. Dhar, D. N. (1981). The chemistry of chalcones and related compounds.
2. Yoshihara, Y. N. (2010) “J. Chem. Pharm. Research”, 2(4), 754-758.
3. Pradeep, S. D., & Mohanan, P. V. (2023). Advancements in Schiff Bases of 1H-Indole-2, 3dione: A Versatile Heterocyclic Compound in Pharmacological Field. *Mini-Reviews in Organic Chemistry*, *20*(1), 45-54.
4. Qiu, J., Tang, B., Ju, B., Xu, Y., & Zhang, S. (2017). Stable diazonium salts of weakly basic amines—Convenient reagents for synthesis of disperse azo dyes. *Dyes and Pigments*, *136*, 63-69.
5. Azzouz, A. S. P., & Al-Niemi, M. M. H. (2011). Influence of structures on the stability constants values for some dyes formation formed by reactions of imines and the diazotized sulphanilic sodium salt. *Iraqi National Journal of Chemistry*, *11*(42), 165-177.
6. Mónica M. Carlsen and Thomas B. Croat "A Molecular Phylogeny of the Species-Rich Neotropical Genus *Anthurium* (Araceae) Based on Combined Chloroplast and Nuclear DNA," *Systematic Botany* 38(3), 576-588, (1 July 2013). https://doi.org/10.1600/036364413X670287
7. Sharma, N., Mohanakrishnan, D., Shard, A., Sharma, A., Saima, Sinha, A. K., & Sahal, D. (2012). Stilbene–chalcone hybrids: design, synthesis, and evaluation as a new class of antimalarial scaffolds that trigger cell death through stage specific apoptosis. Journal of medicinal chemistry, 55(1), 297-311.
8. Ali Mohsin, A. H., Al-Niemi, H., & Mahmoud, M. (2022). Thermodynamic study for the stability of aromatic complexes formation derived from the reaction of 4-dimethyl amino benzaldehyde with diazotized dinitro aniline reagents. *Egyptian Journal of Chemistry*, *65*(2), 421-437.
9. Phan, T. P., Teo, K. Y., Liu, Z. Q., Tsai, J. K., & Tay, M. G. (2019). Application of unsymmetrical bis-chalcone compounds in dye sensitized solar cell. *Chemical Data Collections*, *22*, 100256.

10. Azzouz, A. S. P., & Obed Agha, A. N. (2005). The influence of surfactants and solvents on the stability constant value of some azo dyes formation between oximes and the diazotized Sulphanilic acid salt. *Journal of Education and Science*, *17*(2), 10-16.
11. Navrotsky, A., Mazeina, L., & Majzlan, J. (2008). Size-driven structural and thermodynamic complexity in iron oxides. *Science*, *319*(5870), 1635-1638.
12. Bello, O. S., Alabi, E. O., Adegoke, K. A., Adegboyega, S. A., Inyinbor, A. A., & Dada, A. O. (2020). Rhodamine B dye sequestration using Gmelina aborea leaf powder. *Heliyon*, *6*(1).
13. Jamil, N., Khan, S. M., Ahsan, N., Anwar, J., Qadir, A., Zameer, M., & Shafique, U. (2014). Removal of direct red 16 (Textile Dye) from industrial effluent by using feldspar. *J. Chem. Soc. Pak*, *36*(2), 191.
14. ALSAQA, R., & SULTAN, N. S. (2020). Study of Thermodynamic Properties of Monoclinic Sulfur (Sβ) Under High Pressure Using Three Different Equations of State for the Treatment Scabies in Dermatology. *International Journal of Thermodynamics*, *25*(2), 33-38.
15. Gladyshev, G. P. (2017). Hierarchical thermodynamics: Foundation of extended Darwinism. *Imperial Journal of Interdisciplinary Research (IJIR)*, *3*(2), 2454.
16. Hussein, D. M. M., & Al-Niemi, Y. (2021). Study the effect of acidity function on the kinetic of the two complexes formation produced from the reaction of salicylic acid with two diazotized reagents. *NVEO-NATURAL VOLATILES & ESSENTIAL OILS Journal| NVEO*, 8850-8860.
17. Saleh, M. M., Khemakhem, H., Jassim, I. K., & Al-Saqa, R. H. (2024). Structure and mechanical properties of cermet Ni-Al/MSZ thick coating prepared by flame spraying technique. *Ochrona przed Korozją*.
18. Chen, Z., & Dubinsky, A. J. (2003). A conceptual model of perceived customer value in e-commerce: A preliminary investigation. *Psychology & marketing*, *20*(4), 323-347.
19. Al-Niemi, H., & Mahmoud, M. (2023). Kinetic Study For The Reactions Of Paracetamol With Diazotized (P-Nitroaniline & Sulfanilic Acid Sodium Salt) Reagents. *Egyptian Journal of Chemistry*, *66*(2), 535-542.
20. Knuycky, L. R., Kleider, H. M., & Cavrak, S. E. (2014). Line-up misidentifications: When being 'prototypically Black'is perceived as criminal. *Applied Cognitive Psychology*, *28*(1), 39-46.
21. L. Li, Q. Wang, R. Deng, S. Zhang, and Y. Lu "Transcriptome profiling of blue leaf coloration in *Selaginella uncinata* (Desv. ex Poir.)," *Canadian Journal of Plant Science* 97(4), 580-593, (9 December 2016). https://doi.org/10.1139/cjps-2016-0260