The Influence of Temperature, pH and the Type of Oxime Isomer on the Stability Constant Values of Some Azo Dyes Formations Between Oximes and the Diazotized Sulfanilic Acid Salt

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Abstract

The paper deals with studying the effect of experimental factors on the value of stability constant (K) of the dyes formed by the reactions of aromatic aldoximes as 2-hydroxy benzaldoxime, 2,4-dihydroxy benzaldoxime and 2-hydroxy-1-naphthaldoxime with diazotized sulfanilic acid salt.

Experimentally the following three physical parameters are found to be effective on K as, temperature, pH and type of syn or anti isomer of oxime.

The study includes several topics, one of them is the thermodynamic of dye formation which prove such process is spontaneous and exothermic. The calculated thermodynmic quantities change have a negative values of Gibbs free energy and heat of reaction. They have range average values between 30.1-44.6 and 0.6-59.5 in units of kJ.mole^{-1} respectively, depending on the structure of the azo dye formation. The entropy changes for the complex formation are also mentioned and discussed. The reaction of azo dye formation is based on donor-acceptor mechanism.

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159.5-0.6   44.6- 30.1

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Introduction

In the last two decades, several workers had used the diazotization reaction as an analytical method for the determination of numerous compounds as, N-(1-naphthyl)-ethylenediamine[1,2], 4-aminoantipyrine[3], aniline[4], arylamines-sulphonamides[5], phenols[6] and 1-naphthylamine[7]. Most of these methods are found to be simple, precise and sensitive for the determination of trace amounts of sample.

To our knowledge a few works had been done on the determination of stability constant[8] of diazotization reaction of phenols. This prompted Azzouz[9] et al to deal with the determination of stability constant of some azo dyes formation between phenolic aldoximes and the the diazotized sulphanilic acid salt. A spectrophotometric method[8] is used for the determination of stability constant value for the reaction between aldoxime with diazotized sulfanilic acid salt.

The present investigation is an extension of the last study, it deals with the factors affecting the stability constant of last reaction. Three physical parameters are included in this study, which are found to be effective on the value of stability constant of a dye formation. It is a worthy study, which may open the way to other subsequent future works.

Experimental

Details of chemicals, reagents, the synthesis of syn aldoximes and instrumentation used throughout this work had been stated in our previous communication[9].

The anti aldoximes are synthesized from their syn analogue by standard method[10], with the aid of either dry animal charcoal or HCl gas methods. The purity of any sample is checked by TLC and characterized by UV, IR spectra and melting points as shown in our earlier work[9].

A similar procedure[9] is followed for the determination of stability constant of azo dye formation for syn and antialdoximes with diazotized sulphanilic acid salt at pH values 5.4, 7.4 and 9.

The thermodynamic of dyes formation is measured at five different temperatures in a range 283-323 K by using a standard equations.

Results and Discussion

Earlier works in our laboratory deal with the effect of experimental factors on some physical constants, such as pKa of oximes[12-13] and tautomerisom of Schiff bases[14]. The results obtained encourage the workers to extend the same factors to the stability constants of the dyes formation between syn phenolic aldoxime and the diazotized sulphanilic sodium salt. These factors or parameters are the temperature, pH and the type of syn or anti isomer in oxime. Generally speaking in order to study the influence of any one of the parameters mentioned, the optimal conditions for any dye formation is hold constant for any two parameters, followed by variation of the third one. Such process is repeated in turn until all parameters are included in the study.

In order to clarify the subject to the reader, the following division of results are thought to be necessary.

1. Effect of temperature

The stability[8-9] constants K of azo dyes formation from syn and anti phenolic aldoximes and phenols are evaluated at five temperatures in a range 283-323 K as in Table 1 using an equation :- $K=1-\alpha/\alpha^2 c$ where

α=degree of dissociation of the dye as determined spectrophotometrically by an equation of a form :- $\alpha=A_m-A_s/ A_m$ where A_m

is the absorbance of the dye at optimal conditions

A_s is the absorbance of the dye at stoichiometric ratio of 1:1 donor : acceptor

Table (1) shows an inverse relationship between K and T and a direct relationship between α and T. The variation of the stability constant of any dye with temperature, encourage the workers to evaluate the thermodynamic functions, ∆G, ∆H and ∆S.

The heat of dye formation ∆H is evaluated[15] from Vant Hoff equation of a form:

$$\ln K = \text{constant} - \frac{\Delta H}{RT} \ \ldots \ldots (1)$$

A plot between lnK versus the inverse of absolute temperature from equation (1) for all dyes, using Excel computer programme, shows an excellent straight lines of R^2 range values between 0.9941-0.9992 as shown in Fig. (1-2). Table (1) summarizes all the , K, ∆G, ∆H and ∆S physical parameters evaluated for any dye at 5.4, 7.4 and 9 pH values. An exception to this, the values of standard phenol are calculated at pH 7.4 alone.

Table (1) shows also the close five ∆H values for any dye at the five different temperatures. This mean that ∆H values are independent on the temperatures in a short range between (283-323) K. The negative signs of all ∆H also mean that the process of dye formation is exothermic[26]. The variation in ∆H values of all dyes, adds a clear answer that ∆H value depends on the chemical structure of the dye.

The Gibbs free energy of dye formation is calculated from equation (2) of the form:

$\Delta G = - RT\ln K \quad \ldots \ldots (2)$

The negative signs of all ∆G values of dyes at pH 5.4, 7.4 and 9

give an indication of spontaneous process[15,16].

The ∆S for the dye formation is represented by an equation[15]:

$\Delta S = S_2 - S_1$, where S_2 and S_1 are entropies of dye and oxime with diazotized reagent respectively. Theoretically ∆S value of any dye is expected to possess a negative sign. This is in agreement with the dye formation between phenol and the diazotized group as in Table (1). On the contrary to this, ∆S values for others aldoximes are all positive. This can be explained by considering the following possibilities:

1. The process of azo dyes formation is accompanied by breaking the hydrogen bonding in the oximes. This lead to S_2 value to be greater than S_1, i.e. $\Delta S = S_2 - S_1$ has a positive sign. Actually, the idea of the presence of an intra molecular hydrogen bonding in oximes as 2-hydroxy-benzaldoxime, 2-hydroxy-1-naphthaldoxime and 2,4-dihydroxy-benzaldoxime has been confirmed in our previous finding[11].

2. It is possible that the degree of hydration[12-13] of azo dye formed is less than that of reacting species. The idea of hydration is also accepted, since both dye and reacting oxime molecules contain a hydroxylic groups of phenolic and oxime nature.

Finally, it can be concluded that the two possibilities, individually or in combination, are responsible for producing positive ∆S values of dye formation.

2- Effect of pH

Previous studies[14,17] have shown a clear influence of pH on tautomerism reactions of phenolic Schiff base or phenolic oxime. Other have found that pH influenced the kinetics[18] of numerous reactions. Theses findings have lead the workers

to deal with the influence of pH on the stability of azo dye mentioned before. In order to simplify the subject, the following divisions are necessary.

1. At pH 5.4

Table (1) shows the possibility of evaluation of stability constants of all phenolic oximes with exception of 2-hydroxybenzaldoxime. This is due to the formation[19,20] of nitrilium or phenoxonium ions intermediate at pH listed. Other oximes found in Table (1) are able to form the same ions at lower pH value[12-13]. In other words, the intermediate ions are formed at lower than 5.4 pH value, depending on the basicity of oxime.

The process of nitrilium or phenoxonium ions formation from 2-hydroxy-1-benzaldoxime occurres after the gain of proton by oximes, according to the following mechanism shown in Scheme (1).
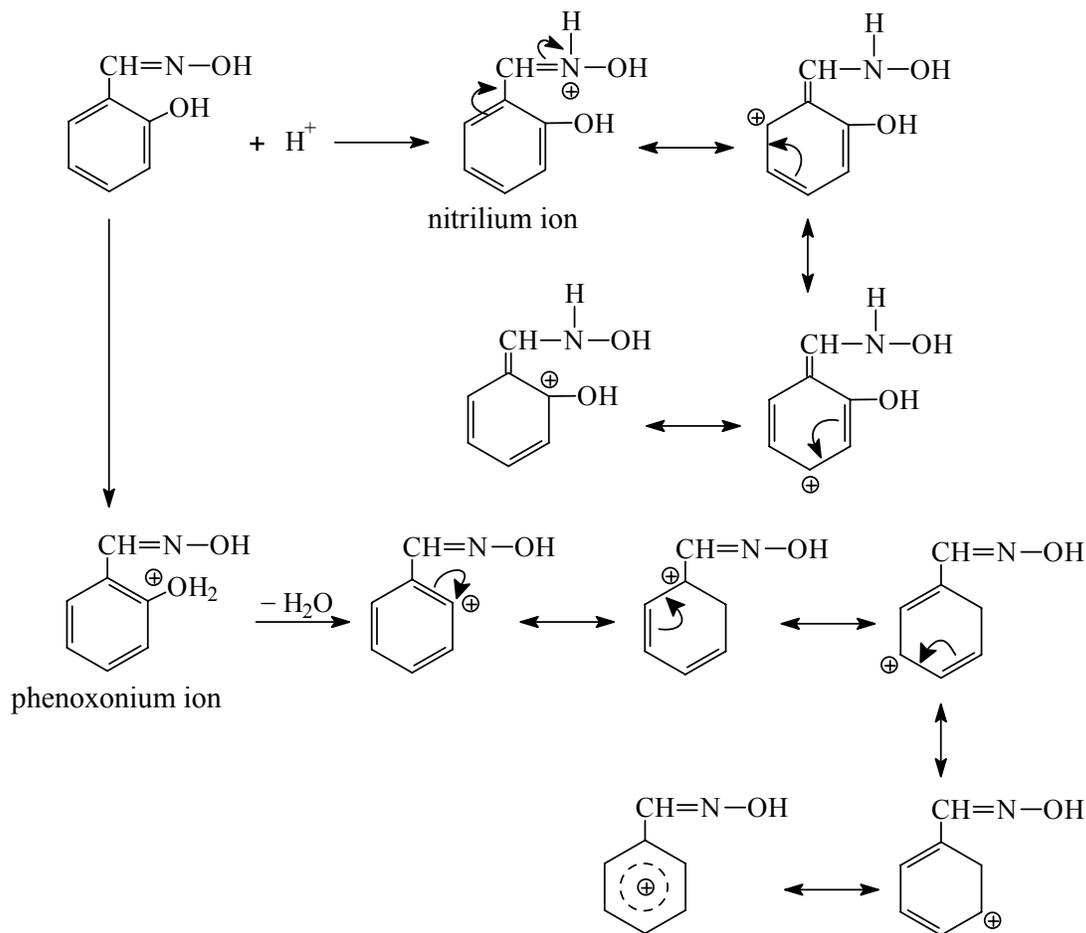
Scheme (1)

This scheme shows that all positions at the aromatic rings are electrophiles carrying a positive charge. This explains the unstable dye formation by repulsion between the two positive nitrilium or phenoxonium ion and the azo group (PhN_2^+) centers.

2. At pH 7.4

Table (1) shows the capability of all oximes to form a stable dye at five different temperatures in a ranging (283-323) K. Moreover, a maximum stability for any dye is obtained at such pH, the reason for that is due to the followings:

1. All oximes found in Table (1) contain an intramolecular hydrogen

bonding between phenolic group and the nitrogen atom of azomethine group. This is evident from our previous study[11], by the measurements of UV and IR spectra. The last lead to the confirmation of the intra molecular hydrogen bonding in oximes by the appearance of additional new UV band at longer wavelength and to a broad IR absorption at $3380cm^{-1}$ which is unaffected by dilution with CCl_4 solvent. The phenoxide ion which is produced from ionization of oxime is expected to be stable by the formation of three resonance structures as shown in our earlier work[9].

The last work shows that the negative charge of phenoxonium ion is produced at ortho and para positions with respect to phenol. This explains the predominate dye formation at para[21] position with respect to phenol, due to the negligible steric effect.

Now when stability constants of the dye formation of 2-hydroxybenzaldoxime and 2,4-dihydroxybenzaldoxime are compared at such pH and constant temperature, one can observe that the value of the latter is greater as in Table (1). A suitable interpretation is given for that by considering the following possibilities:

1. 2,4-Dihydroxybenzaldoxime has a greater number of phenolic group, if compared with the other oxime. Surely, this will increase the electronic density at the aromatic ring as stated[9] above. Therefore, it is not surprising to obtain a greater stability constant value of 2,4-dihydroxybenzaldoxime.

2. 2,4-Dihydroxybenzaldoxime is able to form zwitter ions[22]. This ion is confirmed in such oxime from the following experimental results :
a. The melting points of 2,4-dihydroxybenzaldoxime and 2-hydroxy-benzaldoxime are (188-190) ^{o}C and (61-62)^{o}C, respectively. The higher melting value of the former, means that such oxime is able to form salt formation[22] of higher melting point when compared with 2-hydroxybenzaldoxime.
b. A blue shift[22] is observed to 2,4-dihydroxybenzaldoxime by the addition of a base as in the following:

Actually zwitter ion formation is a phenoxonium ion indeed as shown in other earlier work[9]. This will increase the negative charge density on the aromatic ring, which will increase the stability constant value of the dye.

The higher stability constant value of dye formed from 2-hydroxy-1-naphthaldoxime if compared with 2,4-dihydroxybenzaldoxime and 2-hydroxybenzaldoxime at constant temperature is explained on the bases of greater stability of seven phenoxonium intermediates, having a two aromatic rings in the original oxime as shown in our previous work[9]. At pH 9

Table (1) shows the ability of 2-hydroxy-1-naphthaldoxime and 2-hydroxybenzaldoxime to form dyes at different five temperatures, with the exception of 2,4-dihydroxybenzaldoxime. This is due to the capability of the latter oxime to undergo a tautomerism[14] reaction of a type
enol ⇌ keto.
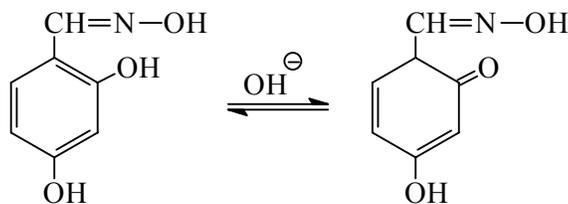
This will result in the destruction of aromatic system of oxime and may be accompanied in decreasing the electronic density at a place of attachment of azo group.

3. Effect of isomerism

The influence of isomerism on the stability constant of azo dyes formation is studied by the comparison of stability constant values of a pair of syn and anti aldoxime having the same chemical formula and at constant pH and temperature. Initially, this requires optimization condition for any anti oxime and this is shown in our earlier study[9] with syn aldoxime. Experimental results show that maximum stability period of five minutes is obtained for a dye formation from anti-2,4-dihydroxybenzaldoxime at pH 7.4 alone. This can facilitate the measurement of stability constant safely. Now, when the pH of the same oxime is changed to 5.4 or 9.0, the stability period is reduced to two minutes. This is not encouraging results leading to ignore the evaluation of stability constant of the dye. Similar results are obtained for anti 2-hydroxybenzaldoxime and the anti 2-hydroxy-2-naphthaldoxime at pH values of 5.4, 7.4 and 9.

The stability constants for syn and anti 2,4-dihydroxybenzaldoxime have a values of 5.87×10^6 and 0.41×10^6 in units L.mole^{-1}, respectively at temperature 283 K and pH 7.4. This indicates a greater stability constant of syn dye if compared with its anti analogue dye. This can be explained by the greater planer[24] structure of syn isomer if compared with the anti isomer isomer, resulted in a greater polymerization of oxime. Finally, the planer polymeric syn oxime may facilitate the motion of electrons or the increase in electronic density on the aromatic ring of oxime. This is subsequent by the greater stability

constant of syn dye complex, according to the donor-acceptor meachinsm[24].

Conclusions

1. The stability[25] of any dye formation from syn aldoxime and sulphanilic acid depends on various factors such as the structure of oxime, temperature, pH and the type of syn or anti isomer of oxime.

2. The enthalpy value of any dye formation depends on the structure of dye. ΔH has a negative sign, which means that the reaction is exothermic[26]. ΔG value also depends on the structure of the dye with a negative sign, which indicates a spontaneous reaction. A suitable interpretation is given for the positive ΔS value. All thermodynamic parameters support the dye formation.

3. The increase in the number of resonance of phenoxide ion and oxime is accompanied by an increase in the value of stability constant. This is clear in the comparison of stability constants of azo dye formation from 2-hydroxybenzaldoxime and 2-hydroxy-1-naphthaldoxime, in which the latter has a greater value as in our earlier work[9].

4. The existence of zwitter ions in 2,4-dihydroxybenzaldoxime at pH 7.4 resulted in an increase in stability constant value. This is clear in the comparison of stability constants of 2,4-dihydroxybenzaldoxime with 2-hydroxybenzaldoxime which gives a greater value of stability constant for the former oxime.

5. Oxime such as 2-hydroxybenzaldoxime is able to produce nitrilium or phenoxonium ion at pH 5.4 as in Scheme (1), resulting to unstable dye. This is

due to the repulsion between two positive centers, the nitrilium or phenoxonium ion and the azo group.

6. The conversion of enol isomer to the keto isomer in 2,4-dihydroxybenzaldoxime resulted in a decrease in stability constant of the dye formed. This is explained on the basis of conversion of hydroxy group in ortho position with respect to oxime group from phenolic form to ketonic one.

7. Syn isomer of oxime in 2,4-dihydroxybenzaldoxime is more planer[23] if compared with its anti analogue. The easier motion of electrons in syn isomer will increase the electron density on the oxime, and is accompanied with an increase in stability constant value of the dye. The last is in accordance with the donor-acceptor mechanism[24] of dye formation.
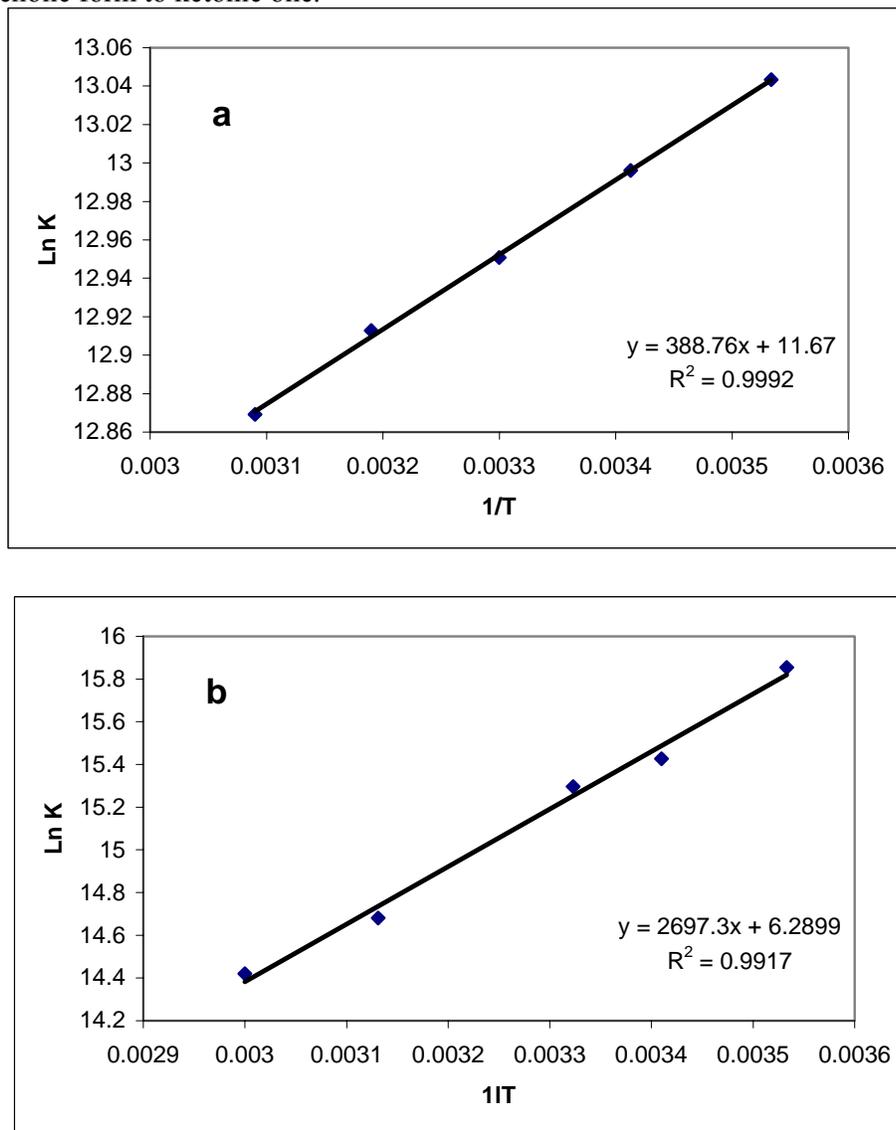

Fig. 1: Effect of temperature on the stability constant of azo dye formation between 2-hydroxy-1-naphthaldoxime with diazotized sulphanilic acid at:
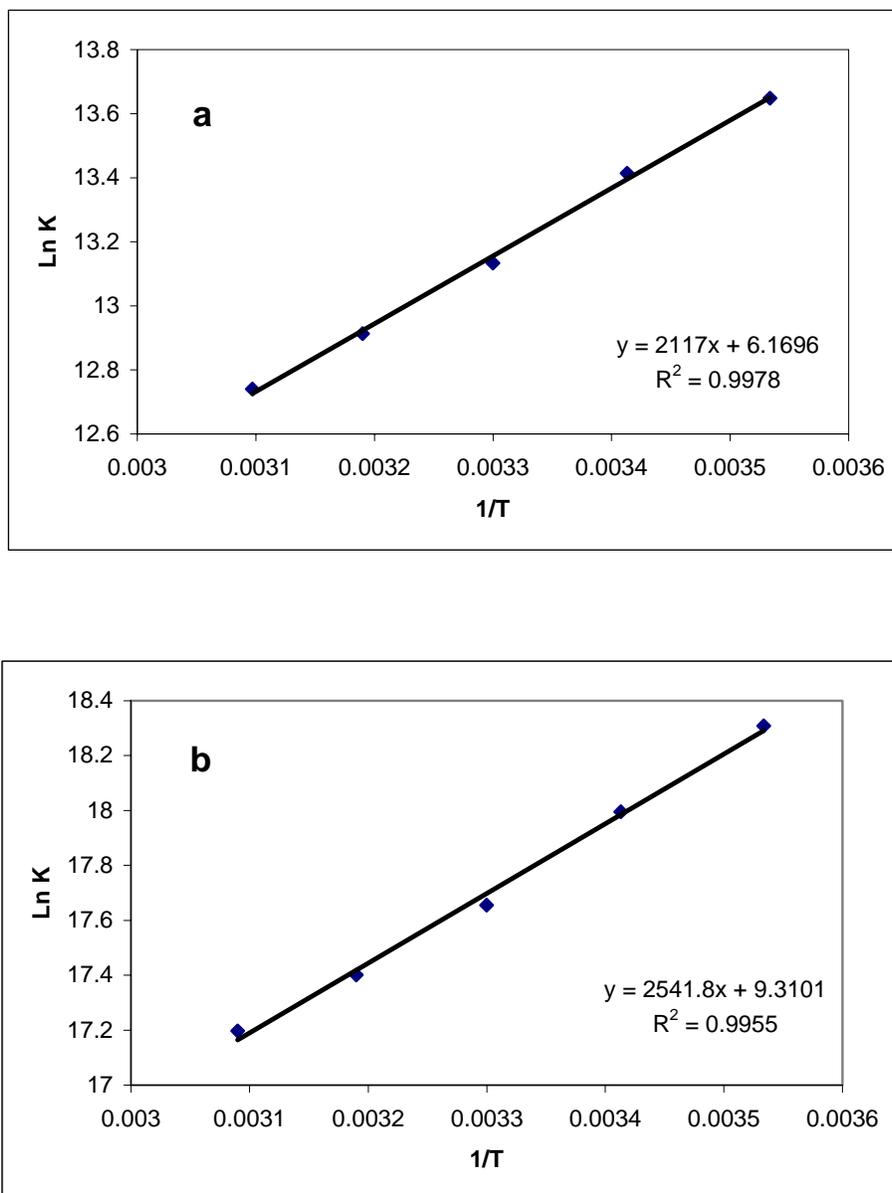   a.   pH 5.4
    b.   pH 9

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Fig. 2: Effect of temperature on the stability constant of azo dye formation
      between diazotized sulphanilic acid with:
   a.   2,4-dihydroxy benzaldoxime at pH 5.4
   b.   2-hydroxy-1-naphthaldoxime at pH 7.4

Table (1): The influence of temperature, thermodynamic parameters and pH on the stability constant values of azo dyes formation of phenol or syn oximes with sulphanilic acid

	PH	T	α	$K\times10^{-3}$ $L.mol^{-1}$	ΔG $kJ.mol^{-1}$	$\overline{\Delta G}$ $kJ.mol^{-1}$	ΔH $kJ.mol^{-1}$	$\overline{\Delta H}$ $kJ.mol^{-1}$	$\overline{\Delta S}$ $J.mol^{-1}.K^{-1}$
Phenol	7.4	283	0.197	517.4	-31.1	-30.1	-58.7	-59.5	-97.2
		293	0.200	500.0	-32.0		-60.5		
		303	0.305	186.7	-30.6		-60.0		
		313	0.440	72.3	-29.4		-59.5		
		323	0.590	27.9	-27.5		-58.9		
2-hydroxy-benzaldoxime	5.4	--	--	--	--	--	--	--	--
	7.4	283	0.212	351.6	-30.0	-32.0	-1.8	-1.8	99.6
		293	0.216	337.3	-31.0		-1.8		
		303	0.218	330.9	-32.0		-1.8		
		313	0.220	322.9	-33.0		-1.8		
		323	0.221	318.5	-34.0		-1.8		
	9	283	0.219	326.8	-29.9	-31.9	-0.6	-0.6	103.3
		293	0.220	323.4	-30.9		-0.6		
		303	0.220	321.2	-31.9		-0.6		
		313	0.221	318.7	-32.9		-0.6		
		323	0.222	315.6	-34.0		-0.6		
2,4-dihydroxy-benzaldoxime	5.4	283	0.180	846.4	-32.1	-33.1	-17.6	-17.6	51.3
		293	0.200	669.2	-32.7		-17.6		
		303	0.226	505.6	-33.1		-17.5		
		313	0.250	405.4	-33.6		-17.5		

Continued

	PH	T	α	$K \times 10^{-3}$ L.mol^{-1}	ΔG kJ.mol^{-1}	$\overline{\Delta G}$ kJ.mol^{-1}	ΔH kJ.mol^{-1}	$\overline{\Delta H}$ kJ.mol^{-1}	$\overline{\Delta S}$ J.mol^{-1}.K^{-1}
		323	0.268	341.3	-34.2		-17.6		
	7.4	283	0.073	5869.2	-36.7	-37.8	-20.0	-20.0	58.8
		293	0.085	4196.1	- 37.1		-19.9		
		303	0.095	3378.4	- 37.9		-20.1		
		313	0.109	2525.4	-38.4		19.9		
		323	0.121	1992.6	-38.9		-20.0		
	9	--	--	--	--	--	--	--	--
2-hydroxy-1-naphthaldoxime	5.4	283	0.207	462.0	-30.7	-32.6	-3.2	-3.2	97.0
		293	0.212	440.7	-31.6		-3.2		
		303	0.216	421.2	-32.6		-3.2		
		313	0.219	405.5	-33.6		-3.2		
		323	0.224	388.2	-34.6		-3.2		
	7.4	283	0.0170	89365.4	-43.1	-44.6	-21.2	-21.1	77.4
		293	0.200	65339.7	-43.8		-21.1		
		303	0.023	46523.8	-44.5		-21.0		
		313	0.026	36067.1	-45.3		-21.1		
		323	0.029	29426.0	-46.2		-21.2		
	9	283	0.056	7677.5	-37.3	-38.1	-22.5	-22.2	52.3
		293	0.068	5009.1	-37.6		-22.3		
		303	0.073	4394.7	-38.5		-22.7		
		313	0.087	2375.0	-38.2		-21.9		
		323	0.110	1830.7	-38.7		-21.8		

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