The influence of surfactants and solvents on the stability constant value of some azo dyes formation between oximes and the diazotized Sulphanilic acid salt

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الخلاصة

يشمل البحث على دراسة تاثير عوامل تجريبية على قيمة ثابت الاستقرار (K) للاصباغ المتكونة من تفاعلات الالدوكزيمات الاروماتية الموضحة اعلاه مع ملح حامض السلفانليك المؤزوت.

عمليا لقد وجد متغيران فيزيائيان يؤثران على قيمة K مثل وجود المواد الفعالة سطحيا (Starch, SDS, CTAB) والمذيبات القطبية الاربعة (water و methanol و ethanol و n-propanol) .

عموما فان قيمة ثابت استقرار الصبغة تحدد لكل من الهيئة التركيبية للالدوكزيم، ثابت العازل الكهربائي للوسط، نوعية المادة الفعالة سطحيا والدالة الحامضية تحت الدراسة.

ABSTRACT

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

Experimentally, two physical parameters have been founded to be effective on the value of K as the presence of three surface active reagents [cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS), starch] and a four polar solvents (water, methanol, ethanol, n-propanol).

Generally, the stability constant value of any dye formation is determined by knowing the structure of aldoxime, the dielectric constant of the medium, the type of surfactant and pH under study.

INTRODUCTION

Molecules and ions that are adsorbed at interfaces are termed surface-active agents or surfactants(1). An alternative expression is amphiphile, which suggests that the molecule or ions has a certain affinity for both polar and nonpolar solvents. These amphiphiles may be predominantly hydrophilic (water-loving), lipophilic (oil-loving) or reasonably well balanced between these two extremes. Surfactants are strongly used in quantitative (2-4) colorimetric analysis for fixation or increasing the stability of the colored formed.

Several workers had observed a great influence of solvents on many reactions as decomposition(1) of drugs, sulphonation(5) of benzene, 1,3-addition reaction(6) between styrene and tetracyanoethylene, hydrolysis(7) of ethyl chloroformate and kinetic(8) isotope effect for a base-catalysed ionization of ethyl nitroacetate with a variety of bases.

As a continutation with two previous communications(9) from this laboratory, the first one deals with the determination of stability constants of some azo dyes formation between phenolic aldoximes and the diazotized sulphanilic acid salt. The second one has a direction of studying the influence of temperature, pH and the type of oxime isomer on stability constant value of some azo dyes formation.

Also this work describes other new physical parameters which are affecting the stability constant value of the azo dyes mentioned, as the effect of surfactants and type of solvents. It is indeed an important study, discussing the influence of these factors on stability constant values of azo dyes formation.

EXPERIMENTAL

Details of chemicals, reagents, the synthesis of syn aldoximes and instrumentation used throughout this work had been stated in our previous communications(9).

A similar procedure(9) is followed for the determination of the stability constant of azo dye formation of syn aldoxime with diazotized sulphanilic acid salt at pH 5.4, 7.4 and 9. The influence of solvent polarity on the stability constant value of the dye is performed by replacing water solvent to other polar solvents as methanol, n-propanol and ethanol at an optimal conditions of the dye formation cited elsewhere(9).

Similar procedure is followed to study the influence of surface active agents as (CTAB), (SDS) and the starch on the values of stability constants. Experimentally 1 ml of 0.1% of aqueous solution for all surfactants are added to the dye at optimal conditions.

RESULTS AND DISCUSSION

A. Effect of surfactant:

Surfactants are protective colloide used sometimes in quantitative colorimetric analysis (2-4) for calculating the stability of complex formation or increasing the strength of colored dyes. These observations encouraged the workers here to deal with a such important physical factor on the stability constant value of the dye between the syn aldoximes as 2-hydroxy-1-naphthaldoxime, 2-hydroxybenzaldoxime and 2,4-dihydroxybenzaldoxime with sulphanilic acid salt. The study is conducted by adding 1 ml of 0.1% surfactants CTAB, SDS and starch to any dye formation at its optimal conditions shown in our earlier communications(9).

Table (1): Effect of surfactants on the values of stability constants (K) of azo dyes formation from syn-2-hydroxy-1-naphthaldoxime with sulphanilic acid salt at temperature 283 K, at different pH

pH	Surface active agent add	λ_{max} (nm)	E_m	E_s	α	$K \times 10^{-6}$ $L.mol^{-1}$
5.4	-	484	0.538	0.427	0.207179	0.46
	CTAB, SDS and starch	-	-	-	-	-
7.4	-	485	1.06	1.042	0.01698	89.37
	CTAB	405	1.260	1.149	0.08809	2.94
	SDS	404	1.062	1.043	0.0179	81.84
	Starch	491	1.086	1.074	0.01104	249.72
9.0	-	484	1.042	0.984	0.05566	7.68
	CTAB	406	1.271	1.162	0.08570	0.31
	SDS	409	1.046	0.984	0.05927	6.72
	Starch	488	1.051	0.994	0.05423	8.08

The last two oximes show a precipation reactions even by decreasing the volume of surfactants or by using a range of volumes between 0.1-1.0 ml. This may indicate a non stable complex formation, hence they are ignored from our study. Table (1) shows the effect of surfactant on the value of stability constant (K) of azo dyes formation from syn 2-hydroxy-1-naphthaldoxime with sulphanilic acid salt at temperature 283 K and at different pH values. In order to simplify the subject, the following divisions are necessary:

1. At pH 5.4:

Actually 2-hydroxy-1-naphthaldoxime is able to form a stable dye with diazotized sulphanilic acid having a stability constant value of 0.46 $\times 10^6$ liter.mole^{-1}. Addition of surfactants in different volumes as shown in the experimental section does not improve or increase the stability of coloured formed, but resulted in decomposing the dye formed. This makes the evaluation of stability constant impossible as shown in Table (1). Hence the idea of surfactant on such oxime at pH 5.4 is no longer to be considered.

2. At pH 7.4 and 9:

Table (1) shows that addition of CTAB and SDS surfactants to the dye formed from oxime 2-hydroxy-1-naphthaldoxime is accompanied by decreasing the value of stability constant. On the contrary to that starch surfactant resulted to an increase in the stability constant value as well as the displacement of the optimum colour of dye to the longer wavelength. This comes in agreement with Gesso(10) finding in a similar study dealing with spectrophotometric determination of some organic compounds in a pharmaceutical preparations via diazotization reaction.

B. Effect of solvent polarity:

Now before studying the influence of solvents on the stability constant of the dye formation between oximes and the azo group of sulfanilic sodium salt, an important believed to deal with solvent polarity. It is known (1,11) that polarity of any solvent is a measure of its dielectric constant. Lowering the dielectric constant decreases polarity of aqueous medium and vice verca. The dielectric constant of four solvents water, methanol, ethanol and n-propanol used in this study, have a values of 78.5, 32.5, 24.5 and 17.1 respectively.

Hence it can be concluded that water has a maximum polarity.

Now Table (2) shows the effect of solvent on the value of the stability constant (K) and wavelength of azo dyes formation from syn oximes with sulphanilic acid salt at temperature 283 K. To simplify the subject the following divisions are necessary at different pH.

1. At pH 7.4:

Maximum stabilities for the dyes are obtained from oximes 2-hydroxy-1-naphthaldoxime, 2-hydroxybenzaldoxime and 2,4-dihydroxybenzaldoxime in solvents water, water and ethanol respectively. In order to interpret the effect of solvents on the value of stability constant of any dye, according to the donor-acceptor mechanism(1) of dye formation, hence the increase in stability constant means a higher electron density on the donor oxime molecule. This is only happen by the ease of ionization of phenolic group in oxime molecule in water and ethanol at neutral pH.

Table (2): Effect of solvent on the value of stability constant (K) and wavelength of azo dyes formation from syn oximes with sulphanilic acid salt at temperature 283 K

Oxime	pH	Solvent	λ_{max} (nm)	$K \times 10^{-6}$ Liter.mole^{-1}
2-hydroxy-1-naphthaldoxime	5.4	Methanol	491	16.5
		n-propanol	488	3.08
		Ethanol	486	26.87
		Water	494	0.46
	7.4	Methanol	490	81.85
		n-propanol	486	9.7
		Ethanol	484	54.35
		Water	484	89.37
	9.0	Methanol	484	7.88
		n-propanol	487	0.73
		Ethanol	485	0.51
		Water	484	7.03
2-hydroxybenzaldoxime	5.4	All four solvents	-	-
	7.4	Methanol	430	0.05
		n-propanol	421	0.07
		Ethanol	431	0.06
		Water	360	0.35
	9.0	Methanol	428	0.80
		n-propanol	402	0.08
		Ethanol	401	0.35
		Water	402	0.33
2,4-dihydroxybenzaldoxime	5.4	Methanol	449	0.41
		n-propanol	452	8.01
		Ethanol	447	10.75
		Water	436	0.85
	7.4	Methanol	450	5.68
		n-propanol	454	8.30
		Ethanol	452	54.16
		Water	446	5.87
	9.0	All four solvents	-	-

The last statement can be understand from the relationship[12]:

$$F = \frac{q_1 \cdot q_2}{\varepsilon r^2}$$

q_1 and q_2 = charge of donor and acceptor.
ε = dielectric constant of the medium.
r = distance between positive and negative ions.

By resonance effect, the negative charge of phenoxide ion produced, is transferred to aromatic ring. This produce a high charge density mainly at para(17) position with respect to phenol group in oxime. This explains the greater stability constant of any dye.

2. At pH 5.4:

At such acidic medium 2-hydroxybenzaldoxime is unable to form a stable dye in methanol, n-propanol, ethanol and water. This is due to the possibility of formation of intermediate (13,14) nitrilium or phenoxonium ion as a positive species. The last is happen after the gain of proton by oxime molecule. This explains the instable dye formation by repulsion between the two positive nitrilium or phenoxonium ion and the azo group PhN_2^+ centers. Also Table (2) shows a maximum stability constant values for the 2-hydroxy-1-naphthaldoxime and 2,4-dihydroxybenzaldoxime in ethanol solvent for the last reason shown in previous section.

3. At pH 9:

At such basic condition a probable conversion (15,16) of phenol group in oximes under study from enol form to keto form. The last is happen to 2,4-dihydroxybenzaldoxime in methanol, n-propanol, ethanol and water solvents, resulting to an unstable dye and an impossible evaluation of stability constant value. On the contrary to that, 2-hydroxybenzaldoxime and 2-hydroxy-1-naphthaldoxime are not subjected to the tautomerism reaction. Hence they give a maximum stability constant values for the dye formed in methanol and for the same reason outlined before.

CONCLUSIONS

1. A spectrophotometric method has been used in the evaluation of stability constant value of a dye formed by the reaction of three aldoximes with sulphanilic sodium salt at pH values 5.4, 7.4 and 9.
2. The stoichiometry of the dye as determined by Job or mole ratio method is found to be of a type 1:1.
3. The stability constant of any dye formation from syn aldoxime and sulphanilic sodium salt is depend on the type of surfactant (CTAB, SDS, starch) and polar solvent (water, methanol, ethanol, n-propanol).
4. The dielectric constant ε of the solvent has a great influence on the ionization energy F of the donor oxime. The decrease in the ε value is accompanied by an increase in F value or an ease ionization of phenolic group of the aldoxime. This resulted to an increase in the stability constant value of the dye at pH 7.4.
5. Polar solvents have different influences on the values of stability constants of the dyes formed by reactions of 2-hydroxybenzaldoxime, 2,4-dihydroxybenzaldoxime and 2-hydroxy-1-naphthaldoxime with azo group. This depends on the pH of the medium and the dielectric constant of solvent.

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