Relation between λ_{max} and p-substituents in some mono-azo dyes

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Abstract

In this project, two series of azo dyes were synthesized by diazotization of para substituted anilines and coupling with 2-naphthol (series 1) and N,N-dimethylaniline (series 2). The wavelength of maximum absorption for the azo dyes of both the series was found with a UV-VIS spectrophotometer. For a particular series, the variation between the inverse of wavelength of maximum absorption with the Hammett coefficient of the para substituent of that particular azo dye was studied.

1. INTRODUCTION

1.1 Azo dyes [1]:-

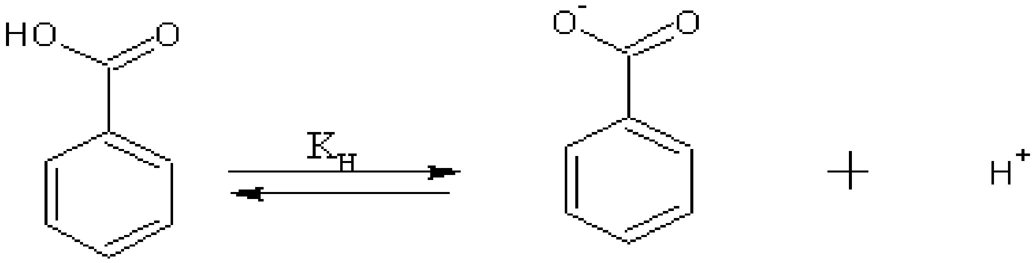
Azo compounds are compounds bearing the functional group -N=N-. IUPAC defines azo compounds as: "Derivatives of diazene (diimide), HN=NH, wherein both hydrogens are substituted by hydrocarbyl groups, e.g. PhN=NPh azobenzene or diphenyldiazene." The more stable derivatives contain two aryl groups. The N=N group is called an *azo group*. The name azo comes from *azote*, the French name for nitrogen that is derived from the Greek *a* (not) + *zoe* (to live).

As a consequence of π-delocalization, aryl azo compounds have vivid colors, especially reds, oranges, and yellows. Therefore, they are used as dyes, which are commonly known as azo dyes. Some azo compounds are used as acid-base indicators due to the different colors of their acid and salt forms. The development of azo dyes was an important step in the development of the chemical industry.

1.2 Hammett equation:-

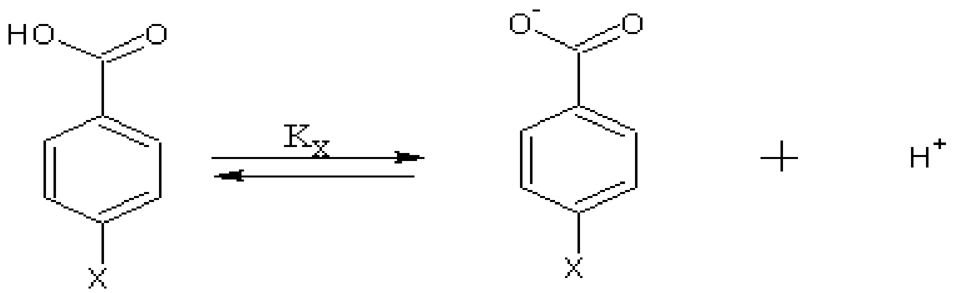
The Hammett equation in organic chemistry describes a linear free-energy relationship relating reaction rates and equilibrium constants for many reactions of meta- and para-substituted benzene derivatives with just two parameters: a substituent constant and a reaction constant [2]. This equation was developed by Louis Plack Hammett in 1937[3] as a follow up to qualitative observations made earlier [4].

The basic idea is that for any two reactions with two aromatic reactants only differing in the type of substituent, the change in free energy of activation is proportional to the change in Gibbs free energy [5]. This notion does not follow from elemental thermochemistry or chemical kinetics and was introduced by Hammett intuitively.



Reaction 1 (Reference **[5])**

(K_H is the equilibrium constant of the corresponding reaction)



Reaction 2 (Reference **[5])**

(Where X is a para substituent and K_X is the equilibrium constant of the corresponding reaction)

$\log (K_X/K_H) = \sigma$ (Hammett coefficient)…………(1)

σ = positive, if X is electron withdrawing group

= negative, if X is electron donating group

From Arrhenius equation,

$k = Ae^{-Ea/RT}$

$\therefore \ln k = \ln A - Ea/RT$

$\therefore \ln k \ \alpha\ \Delta Ea$ (energy)

Now, $\ln k\ \alpha$ Hammett coefficient………………from (1)

$\therefore \Delta Ea\ \alpha$ Hammett coefficient (σ)

Hence, there is a direct relationship between an energy term of p-substituted aromatic compounds with the corresponding Hammett coefficient. In case of azo dyes, there exists an energy term which determines the λ_{max}, and which can be expressed as,

$\Delta E\ \alpha\ (1/\lambda_{max})$

Literature survey was done regarding this topic and the related articles were sourced from Chemical Abstracts.

Since $\Delta E_a\ \alpha\ \sigma$, $1/\lambda_{max}$ is expected to be proportional to σ.

Such a relationship was first described [6] by Russian workers in 1964, wherein they studied solvatochromism in a series of substituted nitro benzenes and Hammett constants. The linear co-relation between Hammett constant σ with the shift of the electronic absorption spectra of some nitro compounds in different solvents was analyzed. Solvatochromism $\Delta\nu$, the difference in ν (max) in n-heptane and ethyl alcohol of nitro derivatives of benzene decreased linearly as σ increased.

They also studied [7] solvatochromy of some substituted p-amino benzene and Hammett constants. The solvatochromic effect was studied for the meta and para substituted derivatives of diazo compounds in ethyl alcohol. The linear relationship was given by

$\Delta\nu = 1640 - 800\sigma$

To the best of our knowledge no further work in this direction was reported after 1964.

Therefore, in this project the relationship between the wavelength of maximum absorption and the corresponding Hammett coefficient of the para substituted azo dyes was studied.

2. EXPERIMENTAL

2.1 AIM: Preparation of azo dyes.

Two series of azo dyes with 2-naphthol and N,N-dimethylaniline as the coupling components and para substituted anilines was prepared. The following aniline derivatives were used:

Aniline, 4-nitroaniline, 4-anisidine, 4-chloroaniline, 4-aminophenol, 4-toluidine, 4-aminobenzonitrile.

A generalized procedure as reported in Ref. 8 was followed for preparing these azo dyes.

2.2 PROCEDURE [8]:

Diazotization:

1. 5 g of the corresponding aniline was dissolved in the required amount of conc. hydrochloric acid and water.
2. The resulting solution was cooled with the help of ice and salt (freezing mixture) and with constant shaking or stirring.
3. A solution of sodium nitrite (equivalent to the amount of aromatic amine used) was added to the above cooled solution at 0°-2°C.

The mixture was stirred at 0°-5°C and completion of reaction was checked by starch iodide paper.

Coupling:

For series 1: β-Naphthol as the coupler:

1. The required amount of β-naphthol was dissolved in adequate amount of water containing an equivalent amount of NaOH.
2. It was stirred in an ice bath such that a temperature of 0°-2°C was obtained.

3. The diazotized amine was added to this coupler solution slowly as a thin stream at 0°-5°C.
4. The precipitated dyestuff was filtered and washed with adequate amount of water.
5. The resulting wet cake was dried in an oven at 60°-65°C.

For series 2: N,N-Dimethylaniline as the coupler:

1. The required amount of N,N-dimethylaniline was dissolved in adequate amount of glacial acetic acid.
2. The above solution was added slowly to the diazotized amine with constant stirring at 0°-5°C.
3. A 2.5N solution of soda ash was added to the above solution very slowly till the reaction mass exhibited a pH of 4-5 (pH paper).
4. The mixture was stirred for half an hour, filtered and the wet cake was washed with adequate amount of water.
5. After adequate washing the wet cake of the dye is dried in oven.

Tables 1 and 2 give the actual amounts of all the reaction materials used.

Note: Since N,N-dimethylaniline is not as reactive as sodium-β-naphtholate towards electrophilic substitution and also the diazonium salts obtained from 4-anisidine and 4-aminophenol are weak electrophiles; the coupling reaction did not take place in these cases at various acidic pH. Thus, no dye is obtained in these cases.

Table 1: β-Naphthol as the coupler (series 1)

Dye No.	Compound (5g)	Moles (mole)	Conc. HCl (ml)	Sodium nitrite (g)	Water (during diazotization) (ml)	NaOH (g)	Soda ash (g)	Water (during coupling) (ml)	β-Naphthol (g)
1	Aniline	0.054	75 ml (2N)	3.73	60	2.16	5	75	5.3
2	4-Nitroaniline	0.036	11 ml+ (11 ml water)	2.5	40	6.7	10	85	5.2
3	4-Anisidine	0.041	50 ml+ (187.5 ml Water)	2.82	20	7.61	11.5	97	5.85
4	4-Chloroaniline	0.039	12 ml+ (40 ml Water)	2.71	19.5	7.31	11	91	5.62
5	4-Aminophenol	0.047	57 ml+ (211 ml Water)	3.18	24	8.63	12	110	6.63
6	4-Toluidine	0.047	70 ml	3.3	53	8.8	12	109	6.8

			(2N)						
7	4-Aminobenzonitrile	0.042	15 ml+ (15 ml Water)	2.95	30	7.9	11	100	6.1

Reference **[8]**

Table 2: N,N-Dimethylaniline (N,N-DMA) as the coupler (series 2)

Dye No.	Compound (5g)	Moles (mole)	Conc. HCl (ml)	Sodium nitrite (g)	Water (ml)	N,N-Dimethylaniline (ml)	Acetic acid (ml)
8	Aniline	0.054	75 ml (2N)	3.73	60	6.84	3.1
9	4-Nitroaniline	0.036	11 ml+ (11 ml water)	2.5	30	4.56	2.1
-	4-Anisidine (coupling reaction was not observed)	0.041	50 ml+ (187.5 ml Water)	2.82	20.15	5.18	2.4
10	4-Chloroaniline	0.039	12 ml+ (40 ml Water)	2.71	19.36	4.96	2.4
-	4-Aminophenol (coupling reaction was not observed)	0.047	57 ml+ (211 ml Water)	3.18	24	5.80	2.75
11	4-Toluidine	0.047	70 ml (2N)	3.3	53	6.00	2.80

12	4-Aminobenzonitrile	0.042	15 ml+ (15 ml Water)	2.95	30	5.31	2.52

Reference **[8]**

Purity of the dyes obtained was checked by thin layer chromatography (TLC) (90:10 hexane: ethyl acetate). In all cases a single spot was obtained. In some cases the melting point of the dye was determined and compared with literature values.

Table 3:

Dye no.	Melting point (reported) °C	Melting point (obtained) °C
1	132 [9]	132-134
2	250 [10]	248-251

References **[9], [10]**

3. RESULTS AND DISCUSSION

Tables 4 and 5 give λ_{max} values (10 ppm in ethyl acetate) of all the dyes prepared along with the corresponding σ values (Hammett coefficient).

Table 4: β-Naphthol as coupler (series 1)

Dye no.	**p-substituent**	**Maximum wavelength λ_{max}(nm)**	**Absorbance at maximum wavelength**	**$1/\lambda_{max}$ (nm^{-1})**	**Hammett coefficient (σ)**
1	-H	470	0.274	0.002128	0
2	$-NO_2$	482	0.104	0.002075	0.78
3	$-OCH_3$	416	0.317	0.002404	-0.27
4	-Cl	473	0.299	0.002114	0.23
5	-OH	416	0.105	0.002404	-0.37
6	$-CH_3$	416	0.339	0.002404	-0.17
7	-CN	476	0.49	0.002101	0.66

Reference **[3]**

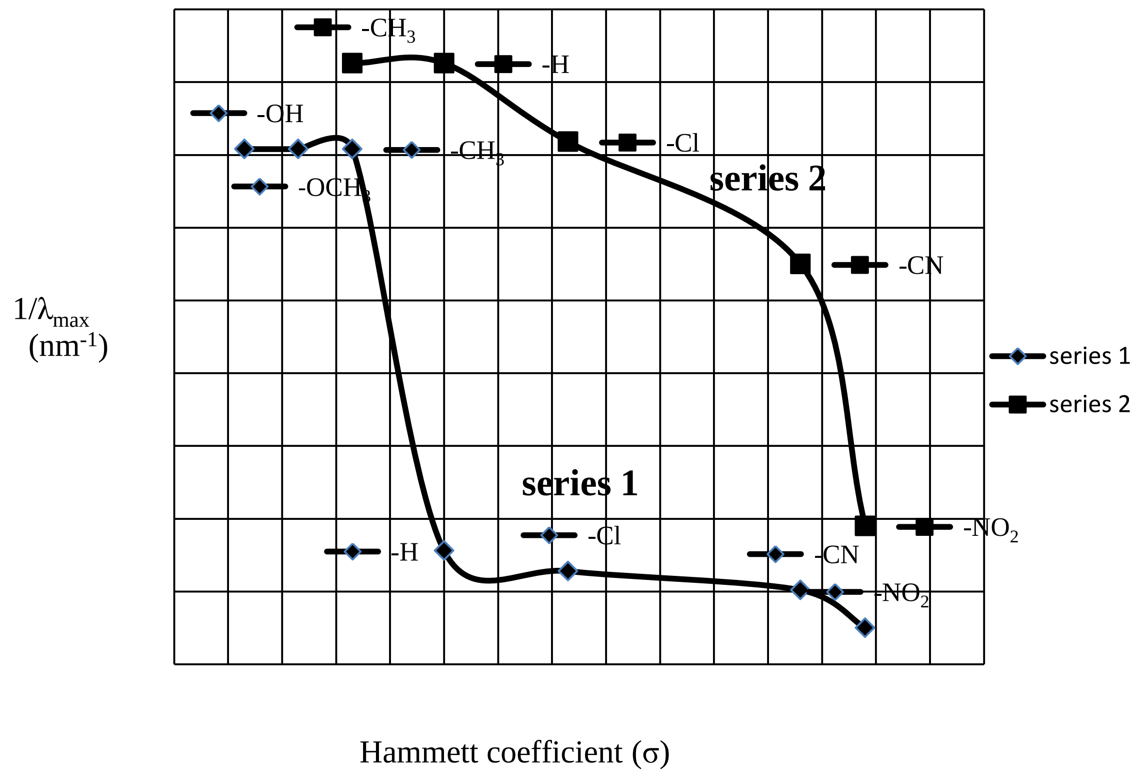
Table 5: N,N-Dimethylaniline as the coupler (series 2)

Dye no.	**p-substituent**	**Maximum wavelength λ_{max}(nm)**	**Absorbance at maximum wavelength**	**$1/\lambda_{max}$ (nm^{-1})**	**Hammett coefficient (σ)**
8	-H	406	3.155	0.002463	0
9	$-NO_2$	466	0.900	0.002145	0.78
10	-Cl	415	2.223	0.002409	0.23
11	$-CH_3$	406	3.654	0.002463	-0.17
12	-CN	430	1.810	0.002325	0.66

Reference **[3]**

Figure3: $1/\lambda_{max}$ vs Hammett coefficient plot

The following graph gives the plot of $1/\lambda_{max}$ vs Hammett coefficient of the corresponding p-substituent for β-Naphthol as coupler (series 1) and N,N-Dimethylaniline as coupler (series 2).



1. From the graph, the slope for series 2 is steeper than that of series 1.

As we compare both the series 1 and 2, the N,N-Dimethylamino (series 2) is a stronger electron donating group compared to the hydroxyl group (series 1) and also the number of double bonds involved in conjugation between the donor and the acceptor is more in series 2 (5 double bonds) than in series 1 (4 double bonds). Therefore, the effect of para substituent is more pronounced in series 2 than in series 1 and hence, the slope for series 2 is steeper.

2. There is a distance between the plots of the two series. For example, aniline when coupled with β-naphthol has λ_{max} at 470nm but when coupled with N,N-dimethylaniline has λ_{max} at 406nm. Hence, there is a red shift when β-naphthol is used as a coupler. This shows that the conjugation is more in case of β-naphthol as it has one more aromatic ring than N,N-dimethylaniline. Therefore, as the conjugation increases, the delocalization of electrons increases and hence, the excited state of the compound becomes more stable and we get a red shift, that is, λ_{max} increases. The same phenomenon is observed in the case of all the derivatives of aniline.

3. The graph for both series 1 and series 2 shows similar behaviour in the 1st quadrant ($\sigma \geq 0$). In this region, we can observe that the plots of dyes formed from diazotization and coupling of aniline, 4-chloroaniline and 4-aminobenzonitrile lie in a straight line, but a sharp fall is observed in the plot of the dye formed from 4-nitroaniline. This shows that the nitro group has a stronger bathochromic effect with respect to its Hammett coefficient as compared with other azo dyes whose plots fall in the 1st quadrant of the graph.

4. In the 2nd quadrant ($\sigma < 0$) of the graph, the inverse of the wavelength of maximum absorption ($1/\lambda_{max}$) remains constant with the variation in Hammett coefficient. Hence, we conclude that for the electron donating para substituents in series 1, the variation of Hammett coefficients with $1/\lambda_{max}$ for the azo dyes is not prominent and the wavelength of maximum absorption remains constant on changing the para substituent from $-CH_3$ to $-OH$ to $-OCH_3$.

5. Another observation is that, as the para substituent is changed from -H to $-CH_3$; in series 1 the λ_{max} for the corresponding dye is decreased from 470nm to 416nm. But no such change in λ_{max} is observed for series 2 which is surprising and

we could not arrive at any suitable explanation.

4. REFERENCES

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