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KINETICS AND THERMODYNAMIC BEHAVIOR OF SOME PREPARED BENZIMIDAZOLE AND CHROMENE DYES ON POLYESTER FIBRE.

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Abstract

Diffusion as a function of temperature of benzimidazole and chromene dyes. It is well known that a carrier is not required for the dyeing of polyester at temperature exceeding 100° C (high temperature dyeing process). This is due to the fact that the diffusion coefficient increases with rising temperature. The extent of this increase was found by measuring exhaustion curves at different temperatures.

Introduction

The dyeing process in case of polyester and wool was carried out near the boiling. It was expected that the dependence on temperature of these diffusion D_T value would be in accordance with the relation:

$$D_T = D_o\, e^{-E/RT}$$

Where D_o= K is a constant. E is the molar energy of activation. T is the absolute temperature and R is the general gas constant. A straight line must be obtained when lin k is plotted against 1/T. The energy of activation E can then be calculated from the slope of this straight line.

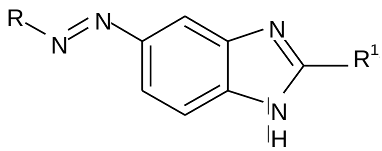
By the same method we can determine the free energy at different temperature by the law (1-6).

$$-\Delta G_T = RT \text{ lin } [\,Df\,] / [D_S]$$

$$\Delta H^o = \Delta G_{100}{}^o + T_{100}\, \Delta S^o$$

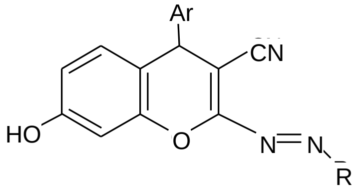
Experimental:

The chemical structures of the synthesized dyes are:



I - III

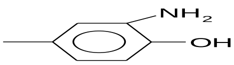
I, R¹ = H; II, R¹ = CH3; III, R¹ = CF3.

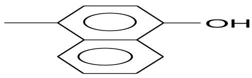


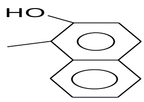
IV & V

IV, -Ar = phenyl; V, Ar = 4-chlorophenyl.

I, II & III:
R=

a, 

; b, 

; c, 

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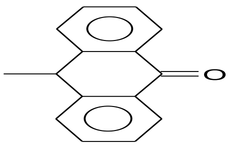
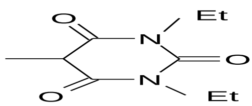
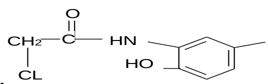
d, 

; e 

;f, 

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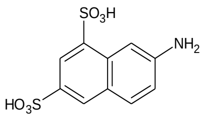
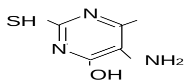
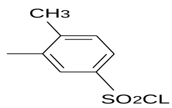
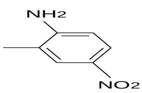
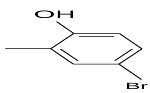
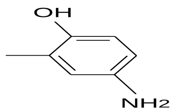
IV : R= a, 

; b, 

; c, 

d, 

; e , 

; f, 

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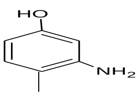
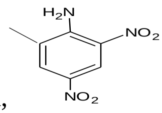
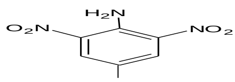
g, 

; h, 

; i, 

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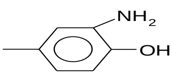
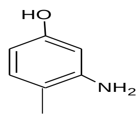
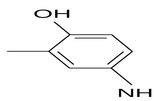
V : R= a, 

; b, 

; c, 

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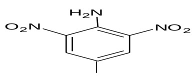
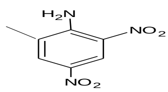
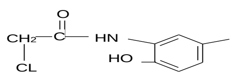
d, 

; e, 

; f, 

The syntheses of these dyes were described in another submitted article(7).

Dyeing Exhaustion curves:

The rate of exhaustion was determined by measuring the optical density of the dye bath solution at different periods up to two hours, using lambada – 3B-spectrophotometer .

II- Materials for dyeing.

Polyester, Polyester woolen type denir 1.4 and wool produced locally at (Misr Rayon Co. Kafr El Dawer and El Mehalla El Kubra), Egypt.

III. Instrumentation and measurements.

1- Melting Point apparatus 2- Spectrophotometric analysis

3- Colour measurements.

Results and Discussions

The rate of exhaustion of the dyeing bath was measured near the boiling by measuring the optical density of the dye bath solution at the previously predetermined λ max for each dye initially and after different periods of time 5,15,25 ………and 120 minutes[8].

$$\% \text{ Exhaustin} = \frac{Aso - Ast}{Aso} \times 100$$

Where Aso = Absorbance at zero time

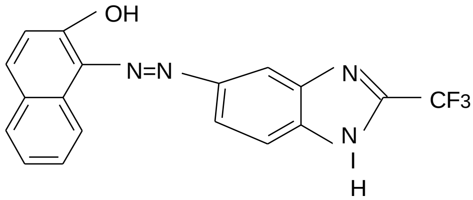
Ast = Absorbance at time (t)

Table (1): % of Exhaustion of disperse dyes on polyester fibre at corresponding different time .

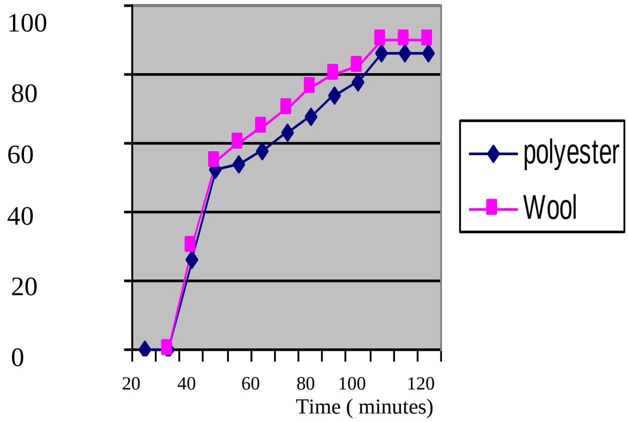
Time Dye No	% fexhaustion on polyester fibre										
	20	40	60	80	100	**Dye No**	20	40	60	80	100
I a	44	56	68	72	82	**f**	43	59	71	75	78
b	40	54	68	72	80	**IV a**	54	68	76	82	88
c	36	50	62	70	74	**b**	50	62	72	79	82
d	38	48	59	70	76	**c**	48	60	70	74	80
e	42	50	63	72	81	**d**	50	58	68	70	78
f	40	56	69	73	80	**e**	50	58	64	74	82
II a	48	60	68	76	84	**f**	52	58	66	76	84
b	42	56	62	72	80	**g**	50	56	64	72	80
c	39	54	62	70	78	**h**	54	68	76	82	88
d	39	54	62	70	78	**i**	52	58	66	78	86
e	40	54	62	70	79	**Va**	50	62	72	79	82
f	35	54	67	71	75	**b**	48	60	70	74	80
III a	52	58	68	78	86	**c**	38	54	67	71	75
b	50	59	67	79	84	**d**	52	58	68	78	86
c	48	58	66	80	82	**e**	50	58	68	76	84
d	42	58	64	74	80	**f**	40	54	62	70	78
e	40	54	62	70	78						

% of exhaustion of group III dyes on wool fibre					
III a	55	65	76	82	90
b	52	62	72	80	90
c	50	60	71	80	90
d	52	62	72	80	90
e	54	64	74	82	92
f	54	70	82	86	88

The results obtained indicate that the dye uptake increased with the increase in time of dyeing. The increased dye up take with the increase of time of dyeing can be attributed to the need of the dye molecule to diffuse inside the fibre and reached to maximum dye up- take.



IIIc



Exhaustion Curves on polyester and wool of III c dye

Fig.,(1)

Table (2): Equilibrium dye up take % and rates of dyeing of PET fibre with disperse dye groups I- V.

Dye No	Polyester Fibre						
	Equilibrium dye up take	$T_{1/2}$ min	Velocity Con. $K\times10^{-3}$ min $^{-1}$	Dye No	M ∞	$T_{1/2}$ min	$K\times10^{-3}$ min^{-1}
I a	82	22.73	14.12	**f**	78	23.25	15.75
b	80	25.0	12.5	**IV a**	88	18.5	18.04
c	74	27.78	12.8	**b**	82	20.0	19.05
d	76	26.32	13.16	**c**	80	20.8	18.75
e	81	23.8	13.29	**d**	78	20.0	13.49
f	80	25	12.5	**e**	82	20.0	19.05
II a	84	20.8	15.8	**f**	84	19.2	19.35
b	80	23.8	13.8	**g**	80	20.8	19.0
c	78	25.6	12.8	**h**	88	18.5	18.0
d	78	25.6	12.8	**i**	86	18.5	18.1
e	79	25.0	12.98	**Va**	82	22.7	14.1
f	75	28.57	11.67	**b**	80	25.0	12.5
III a	86	19.2	17.78	**c**	75	28.5	12.0
b	84	20.0	17.5	**d**	86	19.2	17.8
c	82	20.8	17.2	**e**	84	20.0	17.2
d	80	23.8	13.8	**f**	78	23.25	16.0
e	78	25.0	13.49				

The obtained results for the prepared disperse dyes (I –V) on polyester fibre from table (2) indicate that

i) The maximum dye up take range (74 – 88)% and this indicate that very good dye up take by the fibre .

ii) The T1/2 min for the prepared disperse dyes ranged from (18.5-28.5) this, indicate that good dyeing process on polyester fibre.

iii) The velocity cons. for the prepared disperse dyes ranged from (11.6 – 19.3) this indicates that slow rate for dyeing mechanism good dyeing process.

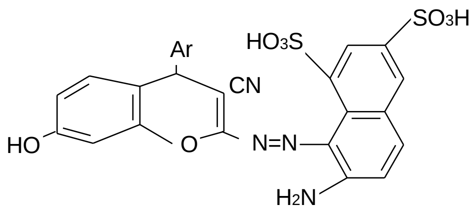
Table (3) :- Equilibrium dye up take % and rates of dyeing of wool fibre with disperse dyes group III..

Dye No	Equilibrium dye up take wool % ($\mu \infty$)	$T_{1/2}$ min	Velocity constant $kx10^{-3}$ min^{-1}
III a	90	18.18	17.46
b	90	19.23	15.2
c	90	20.0	13.88
d	90	19.23	15.2
e	92	18.5	15.44
f	88	18.5	18.04

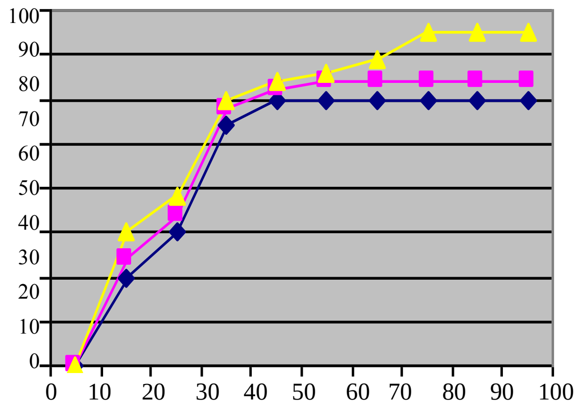
Table (4): - Exhaustion % of disperse dyes I, V by polyester fibre:- at different Temperature

Time Dye NO	Exhaustion %														
	Polyester fibre							Polyester fibre							
	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C	Time Dye NO	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
I a	28	58	67	77	79	80	82	g	25	52	60	64	69	74	80
b	25	54	60	65	69	75	80	h	30	52	60	66	70	78	88
c	28	56	65	68	72	73	74	i	32	53	60	63	68	76	86
d	27	54	62	68	72	74	76	va	25	52	60	66	70	74	82
e	26	53	60	65	69	74	81	b	24	50	60	64	68	72	80
f	24	54	58	64	68	75	80	c	24	50	60	62	65	70	75
II a	30	60	65	70	75	80	84	d	30	50	60	66	70	80	86
b	24	60	67	70	75	78	80	e	28	54	60	64	70	80	84
c	27	56	60	65	70	74	78	f	26	50	58	61	65	70	78
d	27	54	62	66	70	74	78								
e	25	54	60	68	72	76	79	Group III dyes on wool fibre							
f	27	51	52	58	62	68	75								
III a	30	51	60	70	74	78	86	28	58	68	72	75	82	90	
b	26	53	58	60	67	74	84	25	54	60	66	70	75	90	
c	27	52	58	68	70	74	82	30	51	60	70	76	84	90	
d	26	53	59	69	70	74	80	27	54	62	66	71	79	90	
e	24	51	55	60	65	72	78	26	52	60	68	76	79	92	
f	27	51	53	55	58	66	78	32	54	62	69	71	79	88	
IV a	30	54	60	64	69	75	88								
b	28	51	57	68	70	75	82								
c	26	52	55	65	68	70	80								
d	28	51	58	60	67	72	78								
e	26	52	55	60	68	76	82								
f	30	54	60	66	70	76	84								

The results obtained indicate that the dye uptake increased with the increase in temperature of dyeing. The increased dye up take with the increase of temperature of dyeing can be attributed to the need of the dye molecule for high thermal energy to over came the energy barrier of the fibre water interface[9]



IVa dve

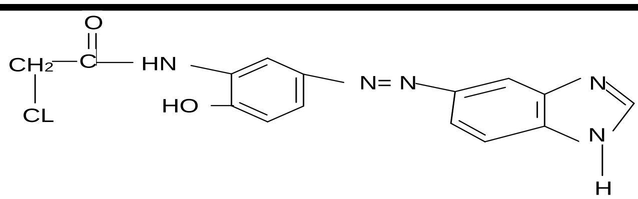


Exhaustion curves on polyester fibre of dye No IVa at different Temp

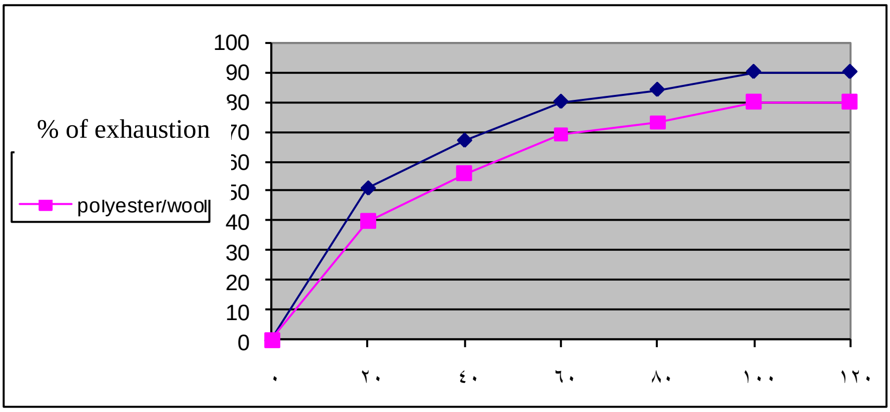
Fig.,(2)

Table (5): % of exhaustion of dyeing of PET/wool, and wool fibre .

Dye No	% of exhaustion on wool fibre						% of exhaustion on polyester/ wool				
Time	0	20	40	60	80	100	20	40	60	80	100
I_f	0	51	67	80	84	90	40	56	69	73	80
II_f		48	65	78	82	85	35	54	67	71	75
III_f		54	70	82	86	88	43	59	71	75	78
IV_d		56	71	84	88	88.5	45	60	73	77	80
IV_e		58	72	86	90	90	47	61	75	79	81



If



Time (minutes)
Exhaustion curves on wool, polyester / Wool, of dye No If
Fig.,(3)

Table (6): Equilibrium dye up take % and rate of dyeing of PET/ wool, and wool fibre with substantial disperse dye I_f , II_f, III_f,IV_d, IV_e at 100c

Dye No	Polyester/wool			Wool		
	Equilibrium dye lake %	$T_{1/2}$ min	Velocity $k.10^{-3}min^{-1}$	M∝ %	$T_{1/2}$ min	Velocity $k.10^{-3}min^{-1}$
I_f	80	25	12.5	90	19.6	14.53
II_f	75	28.57	11.67	85	20.8	15.26
III_f	78	23.25	15.75	88	18.5	18.04
IV_d	80	22.2	16.08	88.5	17.85	19.47
IV_e	81	21.28	17.06	90	17.24	20.14

Table (7): Exhaustion % of substantial dyes I_f , II_f, III_f,IV_d, IV_e by polyester/wool, and wool at different temperature.

Temp Dye No	Exhaustion%											
	Polyester / wool						Wool					
	50°c	60°c	70°c	80°c	90°c	100°c	50°c	60°c	70°c	80°c	90°c	100°c
I_f	54	58	64	68	75	80	58	67	75	78	82	90
II_f	51	52	58	62	68	75	54	64	69	72	75	85
III_f	51	53	55	58	66	78	54	62	69	71	79	88
IV_d	51	54	58	60	72	80	52	57	59	65	73	88.5
IV_e	51	55	65	68	74	81	53	60	70	76	84	90

Thermodynamic behavior of some prepared dyes on polyester fibre [10].

Table (8): Calculation of ΔG, ΔG/T, 1/T for the prepared dyes under investigation.

Dye No	(T)° K	$-\Delta G^{\circ} \times 10^{3}$	$\frac{\Delta G}{T}$	$\frac{1}{T}$
I a	323	0.21	0.65	3.1×10^{-3}
	333	0.47	1.41	3×10^{-3}
	343	0.83	2.42	2.9×10^{-3}
	373	1.13	3.03	2.7×10^{-3}

Table (9) :- Thermodynamic function of some dyes

Dye No	ΔE	- $\Delta G \times 10^3$	$\Delta H \times 10^3$ K.cal.	-ΔS cal ◌̊ K^{-1} mole $^{-1}$
I_a	780	1.13	7.6	87.3
II_a	1050	1.24	8.0	92.4
III_a	1150	1.36	7.35	87.1
IV_a	850	1.94	5.0	64.9
I_f	815	1.04	5.2	62.4

The results obtained from table (**9**) indicate that:

1)- ΔG ranged from 1.04-1. 94 positive value indicate the real dyeing process on polyester fibre sample.

2)- (- Δ S) ranged from 62.4-92.4 cal K^{-1} mole $^{-1}$ high positive value this ◌̊ indicate that the dye molecule inside the fibre is regular and arrangement inside the fibre this module for completing dying process

3)- | ΔH | ranged from 5-8 K cal this indicate that the dyeing process completing by diffusion controlled not by chemical bonding reaction which has the | ΔH| value ranged from 18-27 K .cal.

4)- (-ΔH) has positive value ranged from 5-8 k.cal this indicate that the dyeing process is exothermic process.

Conclusion

From this research of benzimidazole and chromene dyes found that:

- ΔG ranged from 1.04-1. 94 positive value indicate the real dyeing process on polyester fibre sample.

- Δ S ranged from 62.4-92.4 cal K^{-1} mole $^{-1}$ high positive value this ◌̊ indicate that the dye molecule inside the fibre is regular and arrangement inside the fibre, also bonded suggesting module for completion of dying process

-ΔH has positive value ranged from 5-8 k.cal this indicate that the dyeing process is exothermic process.

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