Oriental Journal of Chemistry Vol. **26**(2), 395-408 (2010)

Kinetic study of dyeing acrylic fabrics with basic dyes in presence of organic solvents

A.M. GAMAL[1], M.El-BATOUTI* and N.F. Al-HARBY[2]

[1]Department of Chemistry, Faculty of Science, Al-Azhar University (Girls) Cairo (Egypt).
*Department of Chemistry, Faculty of Science Alexandria University, Cairo (Egypt).
[2]Department of Chemistry, Faculty of Science and Arts, Al Qassim University, Al-Qassim (Saudi Arabia).

(Received: February 10, 2010; Accepted: April 28, 2010)

ABSTRACT

The kinetic of dyeing acrylic fibers with basic dyes in the presence of small amounts of the solvents butanol and 1-4 Dioxane has been studied. The time of half-dyeing was taken as a measure of the rate of dyeing, which was found to decrease with increasing concentration of the solvent in the dye bath. Although acrylic has an additional problem of difficult dye penetration due to its relatively compact physical structure. For a given dye/fiber system, the dye uptake is controlled by several experimental parameters such as temperature, initial dye concentration, and diffusion coefficient. Addition of organic solvents may modify the structure of fabrics causing an increase in the dye ability. Using the three basic dyes (C.I. Basic Red 12, C.I. Basic Orange 21, and C.I. Basic Violet10) , the rate of dye uptakes was studied in absence and presence of the above additives at different time intervals and temperatures (80,90,95 ^oC). The obtained results indicate that the dye uptake increases under the different conditions mentioned. The rate of dyeing is closely related to the diffusion behavior of acrylic fabric. The dyeing rate increases with increasing diffusion coefficient of the dye. The calculated activation energy in presence of solvent gave another evidence for this conclusion. The dye uptake in all cases was found to increase linearly with decrease in the glass transition temperature of the acrylic fibers.

Key words: Basic dyes, acrylic fibers, Butanol, 1-4 Dioxane, Kinetic studies.

INTRODUCTION

100% polyacrylonitrile fabric are usually highly crystalline in which stretched chain molecules are held together strongly by intermolecular hydrogen bonding acting through the nitrile group[1,2].

Acrylic fabric was difficult to dye due to capacitance of physical structure, absence of functional groups and to its high glass transition temperature[3]. To improve these, co-monomer is added or fabric modification is tried used. Various methods of copolymerization have been leading to copolymers containing sulphonic acid groups which impart substantivty for basic dyes. Dyeing of synthetic fibers was found to be difficult also in aqueous system, particularly at lower temperature and normal pressure[4]. This occurs because these fibers are highly crystalline, markedly hydrophobic and do not swell in water. Organic solvents play an important role in dyeing synthetic fibers[5]. They have been employed to swell the fibers and thus decrease the intermolecular attraction forces between the polymeric chains of the fibers[5]. In turn the rate of diffusion of the dyes will be greatly increased inside the fiber. The present paper reports a kinetic study carried out to examine the effect of the addition of the solvents butanol and 1-4 dioxane on the diffusion of Basic dyes.

Recently, the diffusion of basic dyes into acrylic fabric is claimed to be considerably improve by addition of aromatic hydroxyl compounds[6]. The solvent is known to act swelling and/or plasticiging action, the chain molecules becoming highly mobile at the dyeing temperature and hence the uptake of the dye by the fabric greatly enhanced[7]. In order to ascertain the effect on the dyeing kinetics of Basic dyes on acrylic fabrics in a finite bath, we have used the model shown by Fick's Law to obtain various dyeing parameter:

$$D=(\pi r^2/16t)(Ct/C\infty)^2$$

Where :
Ct=concentration of dyeing at each time mol/L.
C∞=concentration of dyeing at equilibrium mol/L.
t=time of dyeing (sec.)
D=apparent diffusion coefficient cm^2/sec.
r=radius of fabric cm.
p=3.14 constant.

Applying the value of each factor above to the Arrhenius equation the activation energy of dyeing (Ea) may be obtained:

$$DT=Do \exp (-Ea/RT)$$

In which DT is the diffusion coefficient at temperature T, and Do is the pre-exponential factor. Results were evaluated on the basis of measurements of time of half-dyeing, diffusion coefficient, activation energy, and dyeing rate .

Chemicals

The chemicals used in the present investigation were; (i)acid such as glacial acetic acid. (ii) base salt as sodium hydroxide (iii) Organic solvents as butanol and 1-4 dioxane. All the reagents were of analytical grade, glacial acetic acid, sodium hydroxide and butanol were obtained from (E.MeRck, Darmstadt), Germany but 1.4 dioxane was obtained from (Riedelde-Haen) Germany.

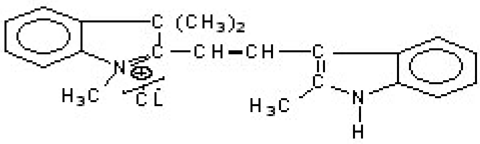
Also the dye solutions for spectrophotometric measurements were prepared by suitable dilution from stock dye solutions in absence and presence of solvents.

Dyestuffs

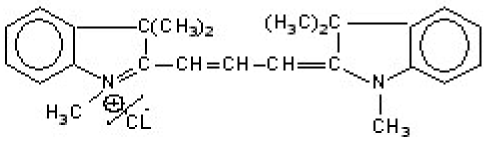
Three different basic dyestuffs obtained from (FBY, Farben, Fabriken, Bayer, A.G., Lever Kusen, Germany) were selected and purified for this investigation [8].Their structures are depicted below.

Fiber

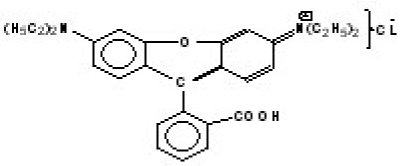
Acrylic fiber was obtained from El-Mahala El Kobra, Egypt. The trade name of this fabric is



C.I. Basic Orange 21 M.wt. =350,89g/mol



C.I. Basic Red 12 M.wt. =390.00g/mol



C.I. Basic Violet 10 M.wt.=479,05g/mol

Orlon. Its construction is count of both wrap and weft = 36/2, warp units = 44/inch, weft units = 43/inch, fabric width = 150 cm and weight of $1m^2$ = 210 gm. and the glass transition Temperature (T_g) is 74.08C.

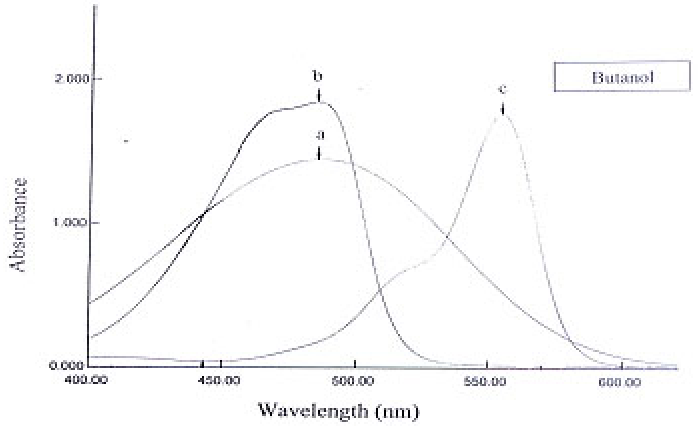
Apparatus

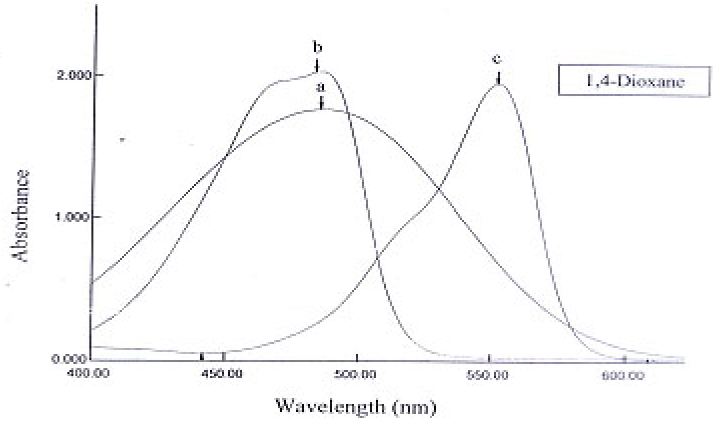
The spectrophotometric measurements were carried out using Beckmann recording spectrophotometer model (UV_VIS) (160A_UV) .

EXPERIMENTAL

Dye solutions were prepared by suitable dilution from stock dye solutions (1.0×10^{-2} mol/dm^3) in absence and presence of solvents. The solvent/ water mixtures were expressed as % volume/volume of (3, 6 butanol) and (5, 10, 1-4 dioxane). All the dye solutions were allowed to stand for 24 hours at T=25°C to attain equilibrium before recording their spectra. The maximum absorbance at longest wavelength for very dilute aqueous dye solution was determined.

Dyeing rates were carried out in stirred thermo stated round bottomed flasks at different temperatures (80,90,95 °C) . The dyeing was also carried out by adding different concentrations of solvents respectively. The samples were removed from the dye bath immediately after each time





a) C.I. Basic Red 12
b) C.I. Basic Orange 21
c) C.I. Basic Violet 10

Fig. 1: Characteristic maximum Wavelength in presence of Butanol and Dioxane

interval. The concentration of the dye solution was determined and the amount of dye on the sample was estimated using a difference method in which the amount of dye on the sample being calculated from the known initial and final concentrations of dye bath from the absorption spectra.

RESULTS AND DISCUSSION

The spectral behavior of the three basic dyes (C.I. Basic Red 12, C.I. Basic Orange 21, and C.I. Basic Violet10) in aqueous and in presence of 1-4 dioxane and butanol were followed in Fig(1) and Table(1). The peak wavelength in the visible region was used in all subsequent spectrophotometric determination ranging between 400-600n.m.

The results revealed that the longest wave length λ_{max} of the dyes used in aqueous solution was observed 485, 483, and 554n.m. respectively.

The presence of solvents shows no very significant effect on the value of the absorption

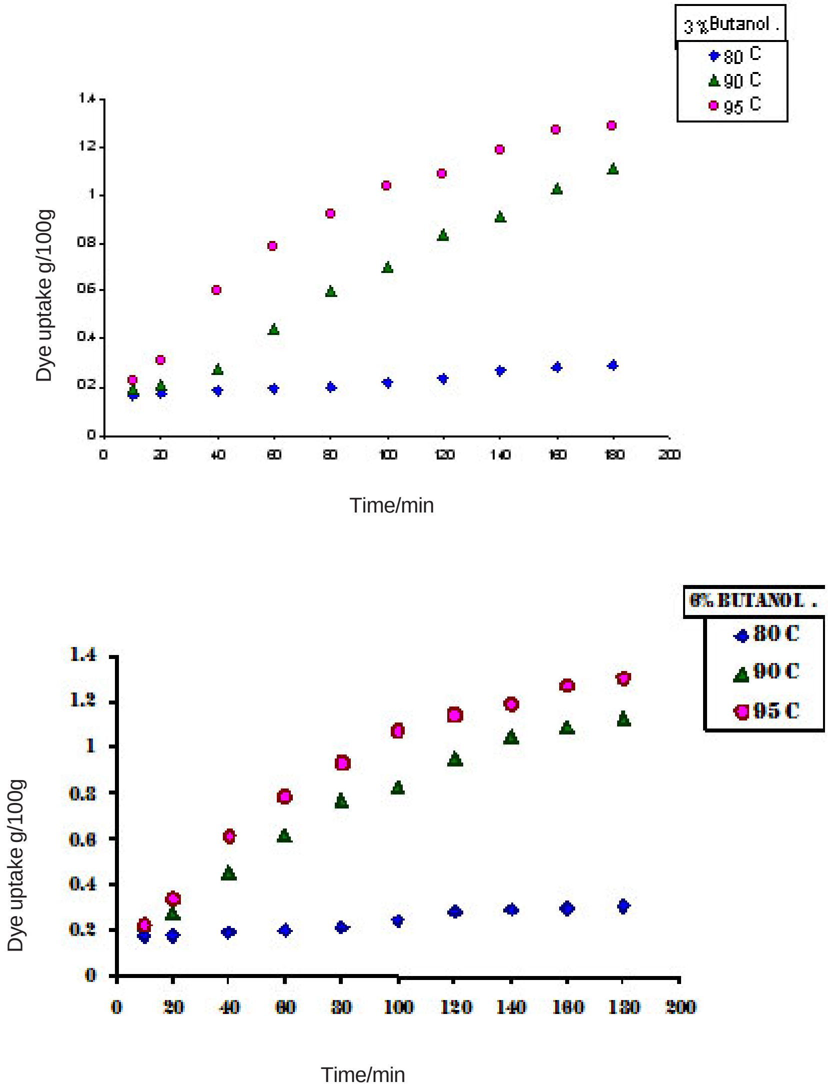


Fig. 2(a) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Red 12 on Orlon in presence of Butanol at different temperatures

spectra of the three utilized dyes. The results obeyed Beer's Law up to the concentrations investigated. Since the solvent leave the extinction at 2.014×10^4, 3,125×10^4 and 11,253×10^4 Lmole^{-1}cm^{-1} for C.I. Basic Red12, C.I .Basic 21, and C.I. Basic Violet 10.respectively.

Dyeing Kinetics

The mechanism of the dyeing of acrylic fibers can be divided into three main steps:

(i) Adsorption of dye on the fiber surface.

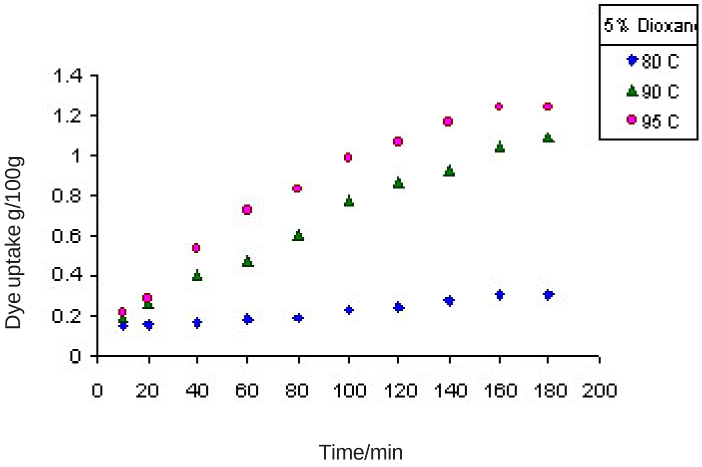
(ii) Diffusion of dye from the surface into the fiber.

(iii) Interaction of the dye with sites in the fiber

The third step occurs so quickly that it has no influence on the kinetics of dyeing. The first two steps could determine the rate of dyeing[9].

The rate uptake of the dyes in absence and presence of solvents

At low temperatures acrylic fibers have a very compact structure which does not allow their constituent atoms to oscillate greatly around their equilibrium positions. As the temperature increases, however, so the mobility of the polymer chains increases, the permeability of the polymer increases proportionately with temperature. Increasing the mobility of the polymer chains probably has two results: the accessibility of dye sites is increased and the ease of diffusion, and hence rate of diffusion, of the dye molecules is increased. These aspects are the subject of research currently being carried out here.



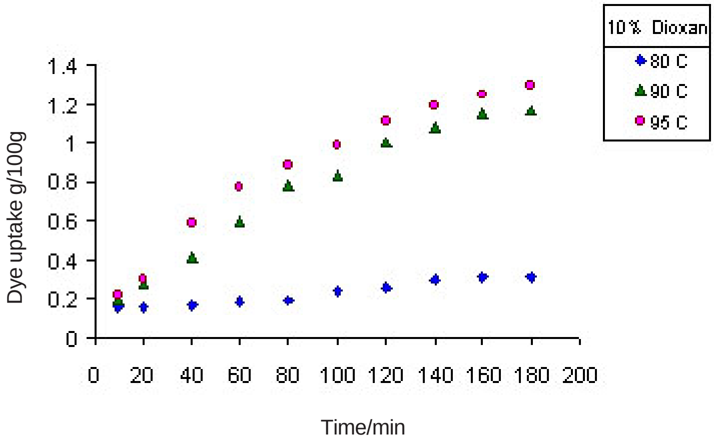


Fig. 2(b) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Red 12 on Orlon in presence of Dioxane at different temperatures

The results in Table(2) and Figs (2) show that the rate of the dye uptake in the modified fabric increases with temperatures and concentrations in absence and presence of solvents. From the data in the table(2) it is seen that the rate of uptake of the three dyes in presence of solvents is greatly increased . The effect of solvents are very pronounced at different temperatures ranked as follows:

1-4 Dioxane > Butanol > water.

These solvents are known to act through their swelling and / or plasticizing action, the chain molecules becoming mobile at the dyeing temperature, and hence the dye uptake of the fiber is greatly enhanced[10,11]. This is in agreement with the observation made by Gur-Arieh *et al.,*[10,11]. According to them, as the plasticizing efficiency of an additive increases, its ability to cause the radial swelling decreases. This suggest that, among the additives used, 1-4 dioxane has the highest plasticizing action on the acrylic fibers. The lateral shrinkage of fiber may be attributed to the difference in the structural aspects of 1-4 dioxane and butanol, since the former is known to swell the acrylic fibers. The reason for such a behavior can be specified by taking glass transition temperature (Tg) of the fiber into consideration. While passing through this temperature range, a considerable change occurs in the physical properties of the fiber. The glass transition temperature of a fiber can be depressed

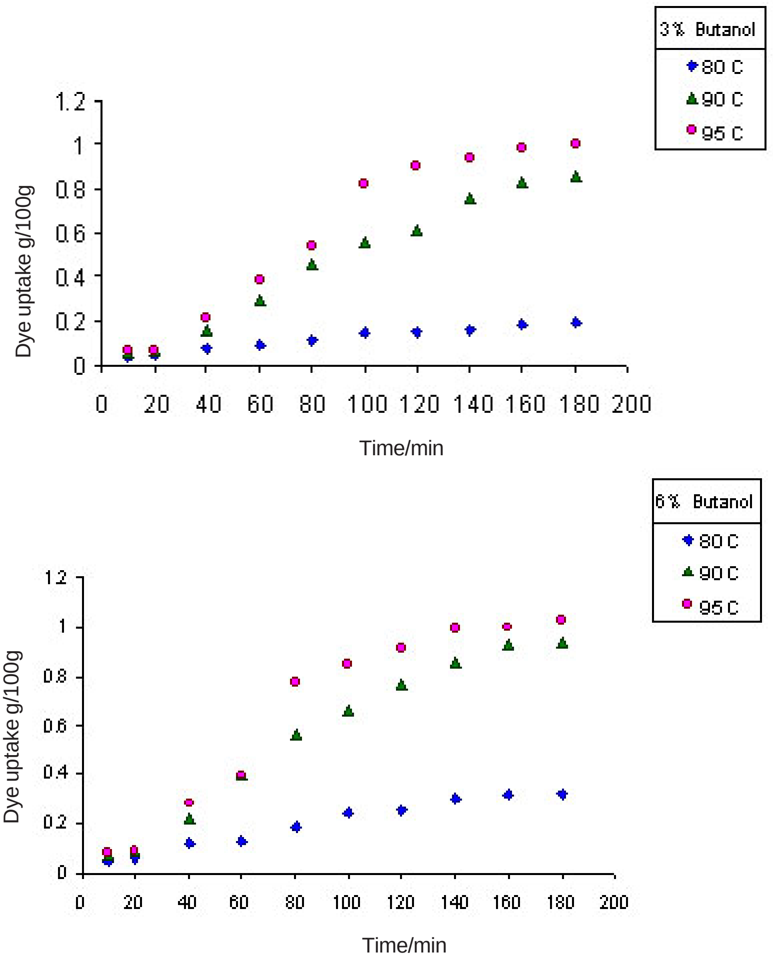


Fig. 2(c) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Orange 21on Orlon in presence of Butanol at different temperatures

by the presence of solvents. The degree of this depression depends on the amount of solvent used and its interaction with the polymer (ie. Fiber). Thus, it may be postulated that addition of 1-4dioxane and butanol decreases the Tg of the fiber and plasticizing effect occurs due to their presence. Penetration of solvent into amorphous region of fiber involves the break-down of intermolecular bonds and produces segmental mobility of polymer chains which results in the lowering of Tg. The mechanism of plasticization also indicates that the inter-chain forces between polymer molecules are reduced by the presence of solvent. So this effect in plasticization of fiber and reduction in Tg which in turn facilitate higher rate uptake[8]. Aggregation of basic dyes may take place in the dyebath itself at lower temperatures. Addition of the solvents, reduce the formation of aggregates of dye molecules, thereby increasing the dye uptake by acrylic fiber.

Measurement of diffusion coefficient in absence and presence of solvents:

The diffusion coefficient D of the three basic dyes used were calculated by using the Fick's law and its solution[12]. The speed of dyestuff diffusion into the fabric determines the rate of dyeing. Diffusion starts above the glass transition point of the fabric (85-95 °C), where fabric molecules acquire enough energy to move. This means, that the fabric softens and dyestuff is allowed to penetrate. The

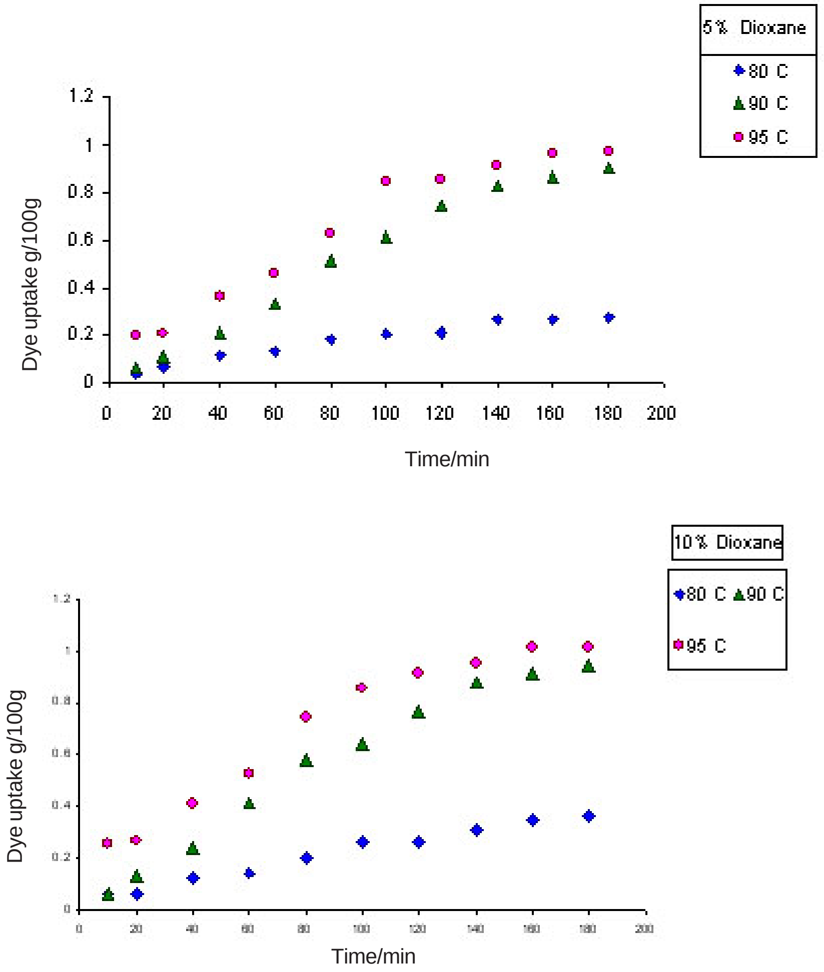


Fig. 2(d) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Orange 21on Orlon in presence of Dioxane at different temperatures

lowering in the (Tg) thereby increased the chain mobility inside the fabric making it more accessible for dyeing[13].The results in Table 2 show that the diffusion coefficient in presence of 6% (V/V) butanol and 10% (V/V) 1-4 dioxane cause an increase in the diffusion of dyes into the modified acrylic fabric than that from the dyebath without any additions. This can be attributed to plasticizing effect which is predominantly responsible for opening up the fabric as compared to the swelling effect. From these results it was shown that the mean apparent diffusion coefficient for the three dyes increased with increasing temperature. Depending on the molecular size of the dye, the solvation of dye molecule due to the presence of carboxylic and hydroxyl groups and the presence of the solvents.

Activation Energy for Dyes

When values of log D were plotted against 1/T, straight lines were obtained Fig.(3) whose slopes gave the values of (– Ea/ 2.303R), from which the activation energy of reaction was evaluated as given in Table(2).From the obtained data the values of activation energies for the three dyes in presence of solvents are lower than in their absence, which could be due to the swelling effect of solvents on

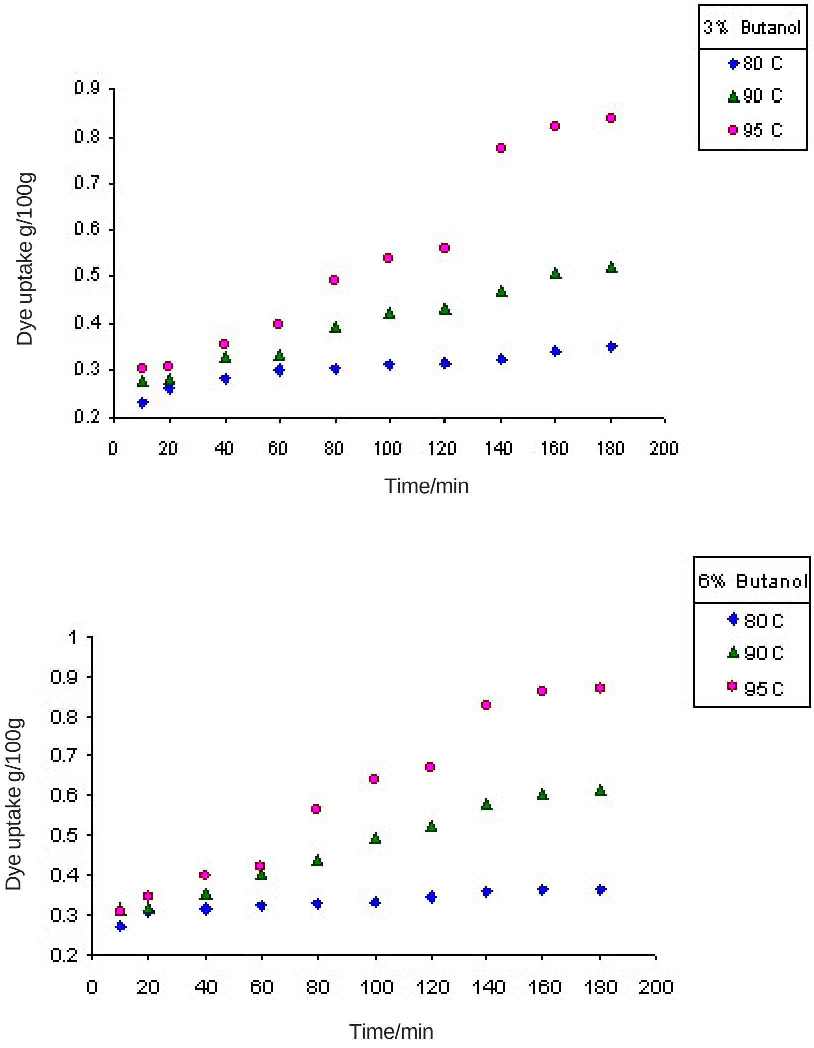


Fig. 2(e) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Violet 10 on Orlon in presence of Butanol at different temperatures

the modified acrylic fabric. As well as weakening of the bonds in the chain molecules which are broken depending upon the ability of particular solvent[14].

The times of half dyeing $t_{1/2}$

The time of half dyeing $t_{1/2}$ is the time required for the fiber to take up half of the amount adsorbed at equilibrium. It is often used as a measure of the rate of adsorption and is given by Hill equation ;

$D=0.063r^2 / t_{1/2}$

D=apparent diffusion coefficient cm^2/sec

r =radius of the fiber cm.

$t_{1/2}$ = time of half dyeing sec.

Values of k and $t_{1/2}$ are given in Table (3) at the different temperatures tested.. As can be seen from this table $t_{1/2}$ for these dyes decreased with increasing temperature, and for adsorption rate constant from the solution k increased markedly. Looking for an explanation for such relationships the activation energies and diffusion coefficients for the adsorption process were determined. For this purpose data for D at different temperatures were fitted to an Arrhenius –type equation.

It has been shown by several authors[14-22] that 1-4 dioxane and butanol act as plasticizer, reduces glass transition temperature of acrylics

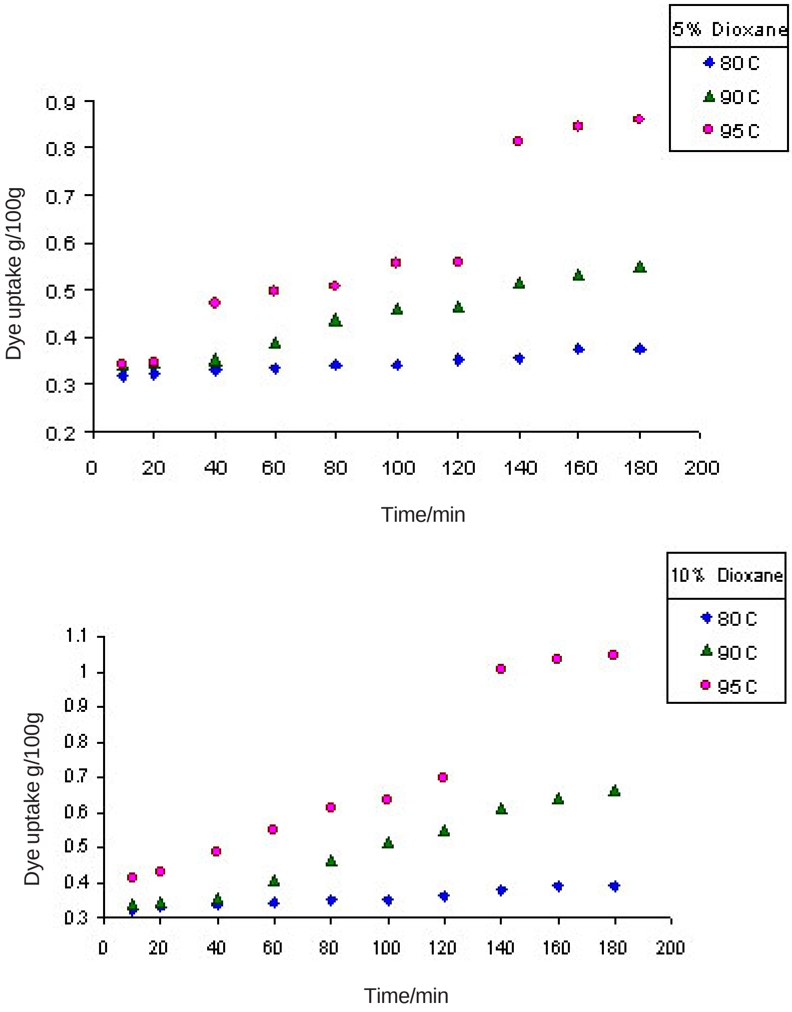


Fig. 2(f) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Violet 10 on Orlon in presence of Dioxane at different temperatures

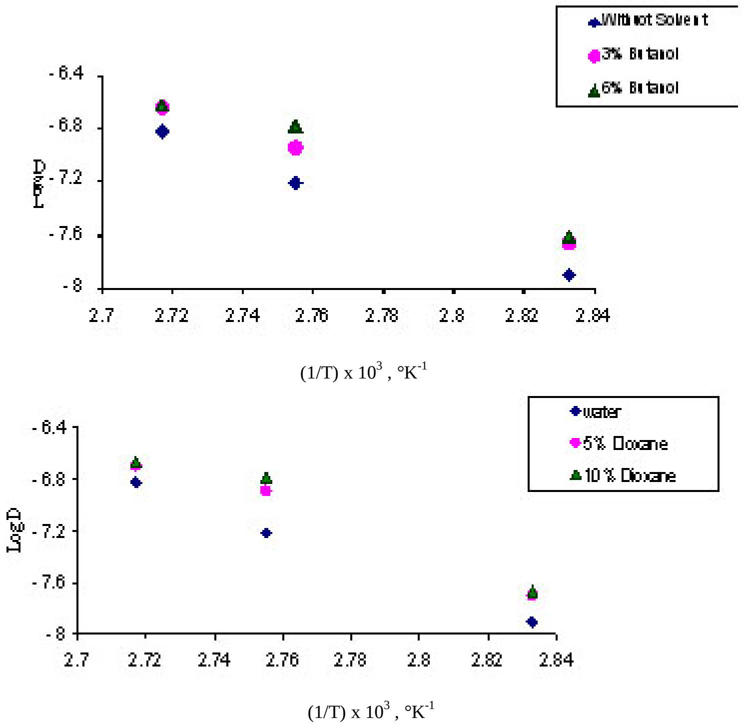


Fig 3(a) : Variation of mean diffusion coefficient with temperatures for C.I. Basic Red 12 in absence and presence solvents

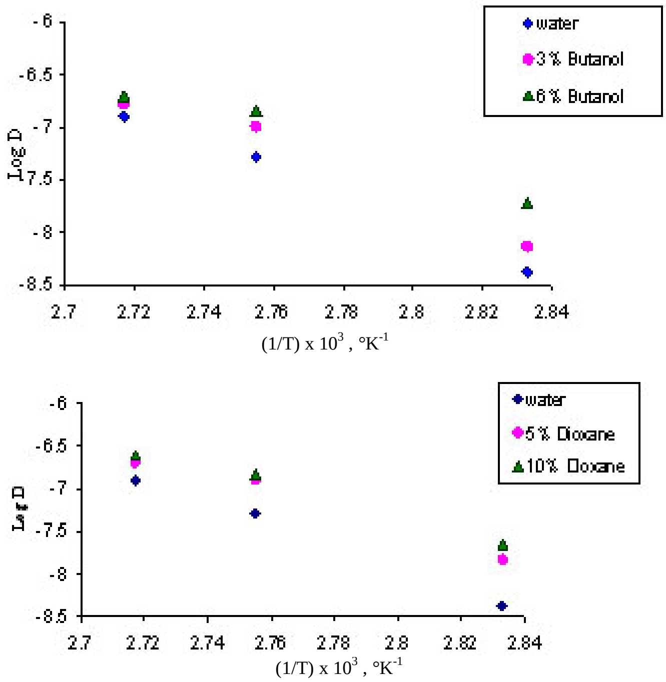


Fig 3(b): Variation of mean diffusion coefficient with temperatures for C.I. Basic Orange 21 in absence and presence solvents

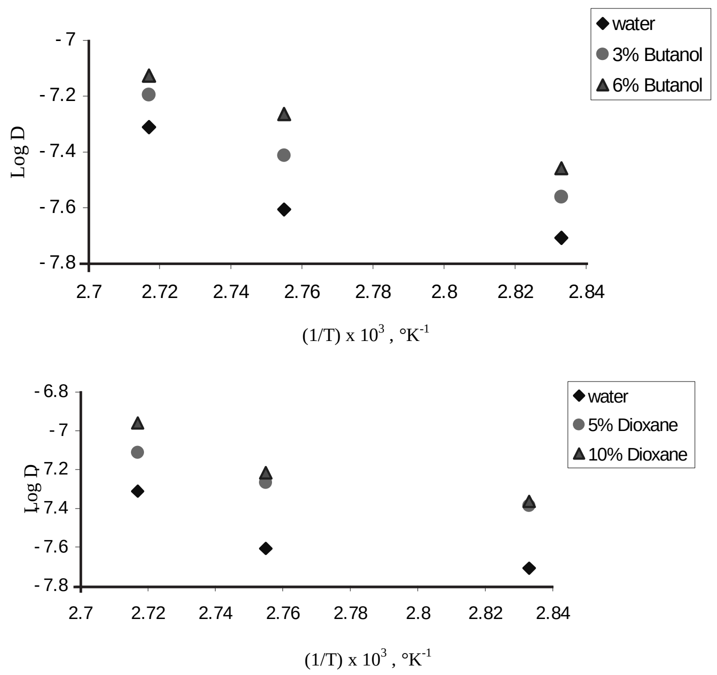


Fig 3(c): Variation of mean diffusion coefficient with temperatures for C.I. Basic Violet 10 in absence and presence solvents

under dyeing conditions and therefore can act as dyeing accelerator. The results show that the diffusion coefficient in presence of 10% 1-4 dioxane and 6% (V/V) butanol causes an increase in the diffusion of dyes into the acrylic fabric than that from the dye bath without any additions. This can be attributed to plasticizing effect which predominantly responsible for opening up the fabric as compared to the swelling effect. From these result it was shown that the mean apparent diffusion coefficient for the three dyes increase with increasing temperature

Table 1: Values of λ_{max} of Dyes used in Different Media

The Dyes	Media	λ_{max}	M.wt.g/mol
C.I.Basic Orange21.	Water	483	350.89
	Butanol	484.4	
	1-4 Dioxane	483.2	
C.I.Basic Red 12.	Water	485	393.00
	Butanol	485	
	1-4 Dioxane	485.2	
C.I.Basic Violet 10	Water	554	479.05
	Butanol	552.4	
	1-4 Dioxane	551.4	

Gamal *et al.*, *Orient. J. Chem.,* Vol. **26**(2), 395-408 (2010)

Table 2: Diffusion Coefficient, Dyeing uptake(k_t) and activation energy (Ea), for Dyes at Different Temperatures and Times in Absence and Presence of Solvents

Temp. (C)		D × 10^7 cm^2/sec	Dyeing uptake (k_t) x 10^2 10 min	20 min	30 min	40 min	50 min	60 min	80 min	120 min	180 min	240 min	Activation EnergyKj mol $^{-1}$/k^o
Water in	80	1.257	0.232	0.304	0.489	0.503	0.557	0.592	0.635	0.885	0.967	1.06	177.936
C.I.Basic red 10	90	6.118	0.244	0.310	0.925	1.277	1.505	2.584	3.275	4.090	4.209	4.562	
	95	15.020	0.424	0.430	1.836	2.936	3.776	6.319	10.161	13.660	15.877	17.611	
6%Butanol in	80	2.478	0.530	0.550	0.592	0.635	0.693	0.814	0.967	1.300	1.034	1.095	161.76
C.I.Basic Red 10	90	16.320	0.715	0.925	1.848	3.022	4.709	5.616	8.435	12.039	14.443	17.401	
	95	23.660	0.730	1.221	3.005	4.962	7.787	13.350	18.705	24.503	48.526	78.990	
10%1-4Dioxane	80	2.149	0.476	0.489	0.523	0.578	0.606	0.783	0.869	1.009	1.077	1.104	161.542
in C.I.Basic Red 10	90	16.430	0.635	0.950	1.584	2.804	4.876	5.650	10.087	13.521	18.942	21.031	
	95	21.820	0.700	1.034	2.796	4.641	6.660	9.522	15.355	24.227	35.885	62.377	
Water in	80	0.420	0.035	0.102	0.233	0.312	0.497	0.559	0.623	0.729	0.867	0.881	244.621
C.I.Basic	90	5.173	0.081	0.318	0.617	1.181	1.958	2.264	2.929	6.274	6.848	6.909	
Orange 21	95	12.730	0.167	0.418	0.763	1.858	4.509	7.190	11.155	19.881	35.881	45.511	
6% Butanol in	80	1.898	0.210	0.295	0.636	0.649	1.035	1.428	1.506	1.928	2.009	2.102	168.033
C.I.Basic Orange21	90	14.300	0.347	0.466	1.253	2.890	5.442	8.159	12.646	20.947	35.918	39.781	
	95	19.780	0.382	0.466	1.715	2.877	13.577	19.625	31.573	80.557	90.809	165.863	
10%1-4 Dioxane in	80	2.237	0.283	0.300	0.630	0.749	1.142	1.577	1.604	1.988	2.376	2.504	115.891
C.I.Basic Orange 21	90	14.690	0.306	0.689	1.411	3.078	5.854	7.452	12.714	23.851	31.841	41.253	
	95	24.950	1.523	1.613	3.023	4.746	11.386	20.424	1.632	45.625	117.923	128.176	
Water in C.I.	80	1.959	0.356	0.367	0.493	0.500	0.520	0.525	0.550	0.656	0.672	0.677	65.529
Basic Violet 10	90	2.475	0.363	0.378	0.500	0.603	0.616	0.729	0.789	0.806	0.966	1.001	
	95	4.883	0.547	0.601	0.619	0.925	0.979	1.017	1.225	1.452	1.614	1.644	
6%Butanol in	80	3.482	0.535	0.624	0.637	0.656	0.667	0.685	0.721	0.749	0.76	0.766	54.800
C.I.Basic Violet10	90	5.441	0.640	0.648	0.743	0.871	0.966	1.147	1.257	1.440	1.542	1.584	
	95	7.478	0.619	0.718	0.856	0.919	1.393	1.684	1.816	2.600	2.841	2.897	
10%1-4 Dioxane in	80	4.323	0.661	0.688	0.699	0.707	0.735	0.738	0.757	0.817	0.832	0.841	36.085
C.I.Basic Violet 10	90	6.074	0.702	0.704	0.740	0.877	1.056	1.221	1.332	1.584	1.702	1.770	
	95	10.960	0.904	0.941	1.116	1.328	1.576	1.684	1.942	3.987	4.291	4.402	

Table 3: Variation of $t_{1/2}$ For Basic dyes in Different Media

Solvent	$t_{1/2}$, min. x 10^2		
	80 °C	**90 °C**	**95 °C**
C.I. Basic red 12			
Water	12.029	2.471	1.007
3% Butanol	6.854	1.321	0.672
6%Butanol	6.102	0.926	0.639
5%1-4 Dioxane	7.504	1.172	0.746
10%1-4 Dioxane	7.036	0.920	0.693
C.I.Basic Orange 21			
Water	35.983	2.923	1.188
3% Butanol	20.377	1.470	0.906
6%Butanol	7.966	1.057	0.764
5%1-4 Dioxane	10.182	1.191	0.746
10%1-4 Dioxane	6.759	1.029	0.606
C.I.Basic Violet 10			
Water	7.718	6.109	3.096
3% Butanol	5.500	3.907	2.370
6%Butanol	4.432	2.779	2.022
5%1-4 Dioxane	3.690	2.791	1.959
10%1-4 Dioxane	3.498	2.489	1.380

CONCLUSION

The purpose of this study is to explore the effect of dyeing kinetics of basic dyes on acrylic fabrics in presence of solvents. The results indicate that as the temperature and time is increased, the equilibrium absorption and rate constant increase, while the activation energy decreases. Furthermore, all the measures of dyeing indicated that acrylic fibers are mainly dependent on the fiber properties itself, the dyes structure and its molecular weight, Although there was significant analysis of the effect of temperature(80-95°C), time (10-180min.), and solvents(butanol and 1-4 dioxane)on the migration of several dyes Orlon–filament fiber has shown that temperature and solvents are the most important variable in controlling migration. The rate of dyeing is closely related to the diffusion behavior of acrylic fabric.

The dyeing rate increases with increasing diffusion coefficient of the dye. The calculated activation energy in presence of solvents gave another evidence for this conclusion.

REFERENCES

1. P. Ghosh. “Polymer Science and Technology, Plastics, Rubbers, *Blends and Composites*”, 2nd., Tata MeGraw-Hill, New Delhi, (2002).
2. P. Ghosh, “Fabric Science and Technology” Tata McGraw Hill, New Delhi, (2004).
3. A.K.Samant and D.Das, *J. Colrage,* 17 1992).
4. A. M. El Naggar,A.M. Marie,M. H.Zohd and A. A. Miligy, *American Dyestuff Reporter,* **85**: 85 (1996).
5. R. H. Symm, *Textile Chemist and Colorist*, **1**: 161 (1969).
6. H.B. Sallam, *Bull. Fac. Sci.* Zagazig Univ., **16**(2): 48-60 (1994).
7. G.A. Zeev amd C.I. Whferd, *J.S.D.C.*, **90**: 12

(1974).
8. J.Cegarra, *J.S.D.C*; **87**: 149 (1971).
9. D. Balmforth, C.A Bower and Gulons , J.S.D.C., **80**: 577 (1964).
10. Z.Gur-Arieh and W.C. Ingamells, J.S.D.C., **90**: 12 (1974).
11. W.C.Ingamells, Z. Gur-Arieh and R.H. Peters, *J. Appl.Polymer Sci*., **20**: 41 (1976).
12. T.K.Sadhu, B.G. Agarwal, P.A. Desai, and P.A. Patel, The Indian Textile J. January 90 (1997).
13. Crnak, "The mathematic of diffusion "Clorndn, Oxford, (1956).
14. H. Emsermann. *Amer, Dyestuff, Rep. Agu.* 48 (1996).
15. Jui-Chi Chem. And Cheng. *Chi Chen. Text., Res. J.*, **70**(4): 311 (2000).
16. Rosenbaum, *J.Poiy, Sci, Part A*, **3**: 1949 (1965).
17. Beal , Dickenson and Bell House. *J.Soc. Dyer* **2**(0)76: 333 (1966).
18. Balmith , Bowers, Bullington ,Guion and Roberts, *J.Soc.Dyers:* **1**(0)82: 405 (1966)
19. A.M.Gamal and G. El Mohamady, *Al Azhar Bulletin of Science*, **15**(1): 69 (2004).
20. D.C. Phillips, J.Taylor, R. Lakhanpal, J. Scotney and G. Bevan, *Coloration Technology* , **117**: 147 (2001).
21. S. A. Abo-Farha, A.M.Gamal, El S. H. Gomaa and N.A. Badawy, *Al-Azhar Bull Sci.* **14**(1): 161 (2003).