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Solvent assisted dyeing of acrylics with basic dyes

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ABSTRACT

Acrylic has an additional problem of difficult dye penetration due to its relatively compact physical structure. Addition of benzyl alcohol 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 additive at different time intervals and temperatures (80,90,95 ^{o}C).The obtained results indicate that the dye uptake increases under the different conditions mentioned. The highest dye exhaustion was obtained using 2%(V/V) benzyl alcohol/water mixture this was attributed to the increase in the accessibility of the acrylic fabrics in presence of benzyl alcohol. The rate of dyeing is closely related to the diffusion behavior of dyes. 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. It is observed that optimum limit of benzyl alcohol concentration varies from dye to dye and is closely related to its molecular size. The obtained results indicate that benzyl alcohol gave a maximum increase in dye uptake, even at a low concentration.

Key words: Basic dyes, acrylic fibers, benzyl alcohol, Kinetic, pH.

INTRODUCTION

The dyeing of acrylic fibers using certain organic solvents in very small amounts in an aqueous dye bath has been studied previously by Gur-Arieh and Ingamells[1,2]. They have shown that the addition of benzyl alcohol to the dye bath increases the rate of diffusion of dye into the fibers and related this behavior to the plasticizing effect of the solvent. The extent to which the solution of a particular plasticizing agent will reduce the glass transition temperature of the acrylic fibers depends on the amount adsorbed as well as the chemical structure of the plasticizing molecule[3].Benzyl alcohol when added in small quantities in the dye bath, has been shown to improve the basic dye uptake by the acrylic fibers[4,5]. Acrylic fabric often shows difficulties in producing penetration dyeing. By incorporating benzyl alcohol in the dye bath, it is possible to get deeper shades[6].Studies on solvent treatment of synthetic fabrics reveal that by suitable choice of a solvent, the chemical structure of the fabric can be modified in order to effect an increase in dye ability. Also in the case of acrylic fabrics benzyl alcohol bring about the structural changes which are reflected in the increase of the dye uptake[6].These solvent systems allow a continuous change from the polar, hydrogen-bonding character of benzyl alcohol to the solvent characteristics of the non-polar dioxane. The basic nucleophiles may be expected to become highly reactive in non-polar dioxane owing to the lack of hydrogen bond stabilization. In the present paper we report the results on the dyeing of acrylic fibers with basic dyestuffs in the presence of benzyl alcohol in the dye bath to improve the fabric dye ability.

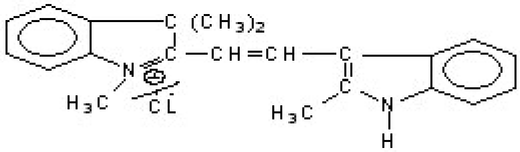
Chemicals

The chemicals used in the present investigation were; (i)acid such as glacial acetic acid. (ii) base salt as sodium hydroxide (iii) Organic solvent as benzyl alcohol. All the reagents were of analytical grade.

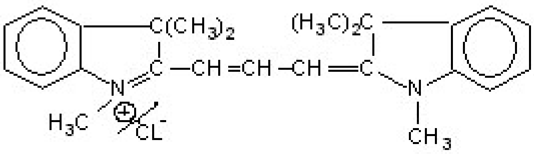
Also the dye solutions for spectrophotometric measurements were prepared by suitable dilution from stock dye solutions in absence and presence of benzyl alcohol.

Dyestuffs

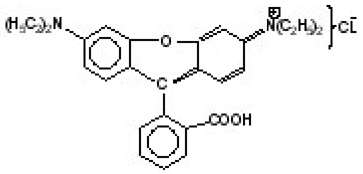
Three different basic dyestuffs obtained from (FBY, Farben, Fabriken, Bayer, A.G., Lever Kusen, Germany) were selected and purified for this investigation[7].Their structures are depicted below.



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

Fiber

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

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

b) For pH –meter model 211 made in Portugal was used. The pH of the dye bath was maintained from (2.97 – 5.95) for three dye stuffs with the help of acetic acid.

EXPERIMENTAL

The intials concentrations of dyes (3.0 x 10^{-4} mol/dm^3) were prepared by suitable dilution from stock dye solutions (1.0 x 10^{-2} mol/dm^3) in absence and presence of benzyl alcohol with molar ligquor ratio (MLR) 1 : 100. The solvent/ water mixtures were expressed as % volume/ volume of (1%,2%)V/V benzyl alcohol. 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 thermostated round bottomed flasks at different temperatures (80,90,95°C) .The dyeing was also carried out by adding different concentrations of benzyl alcohol (1% 2%)V/V respectively. The samples were removed from the dye bath immediately after each time 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 Benzyl alcohol was reported in Fig(1) and Table(1). The peak wavelength in the visible region was used in all subsequent spectrophotometric determination

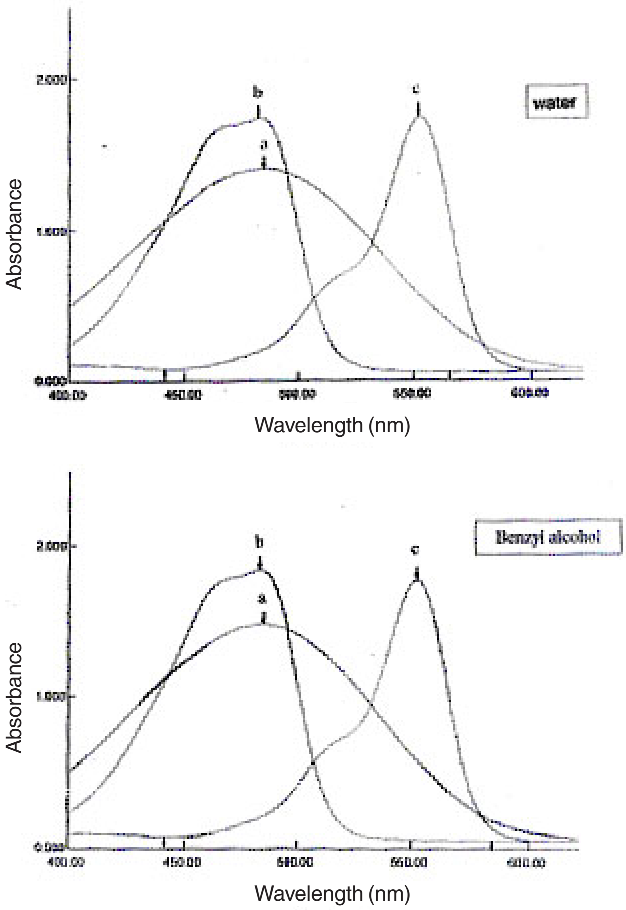


Fig. 1: Characteristics maximum wavelength in absence of solvent and presence of Benzyl alcohol: a) C.I. Basic Red 12, b) C.I. Basic Orange 21, c) C.I. Basic Violet 10

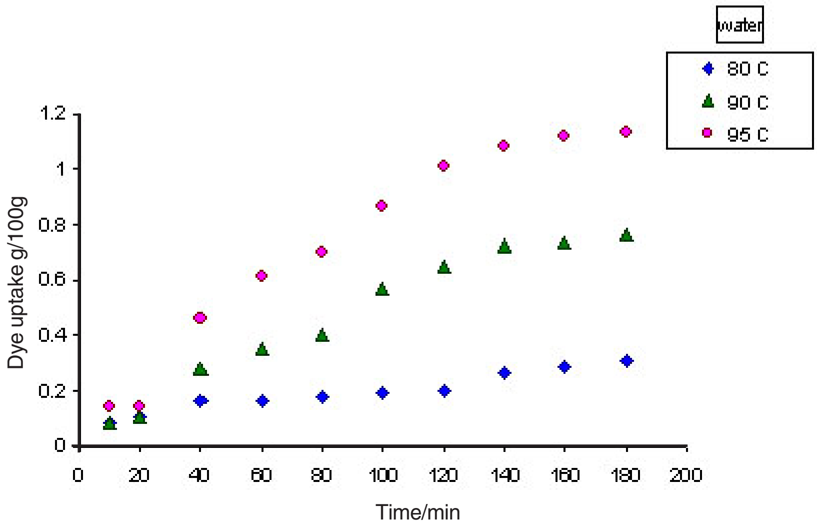


Fig. 2(a): The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Red 12 on Orlon in water at different temperatures

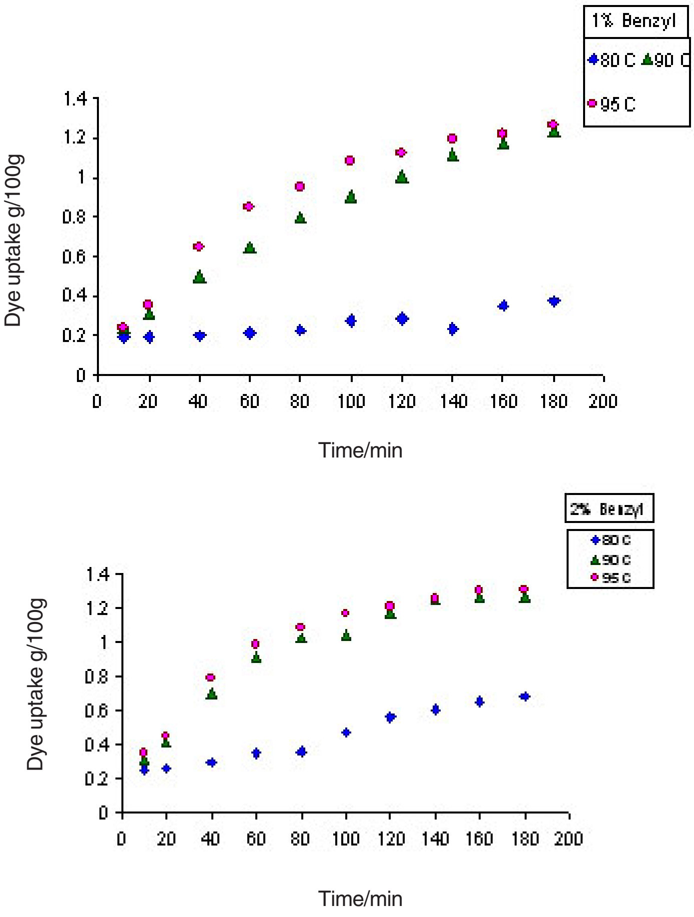


Fig. 2(b): The Relation between dyeing uptake (g/100 g) and time (min) of C.I. Basic Red 12 on Orlon in presence of Benzyl alcohol at different temperatures

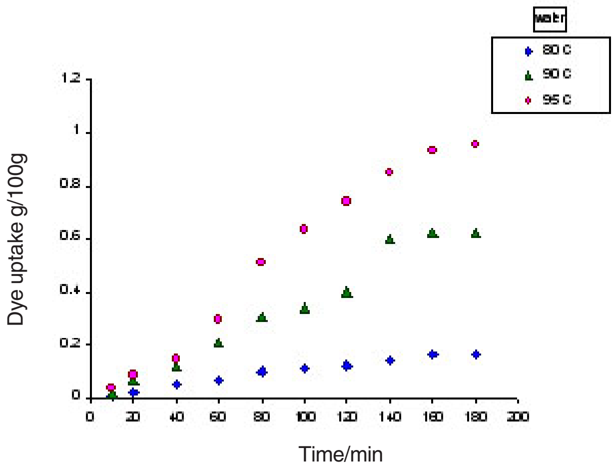


Fig. 2(c) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Orange 21on Orlon in water at different temperatures

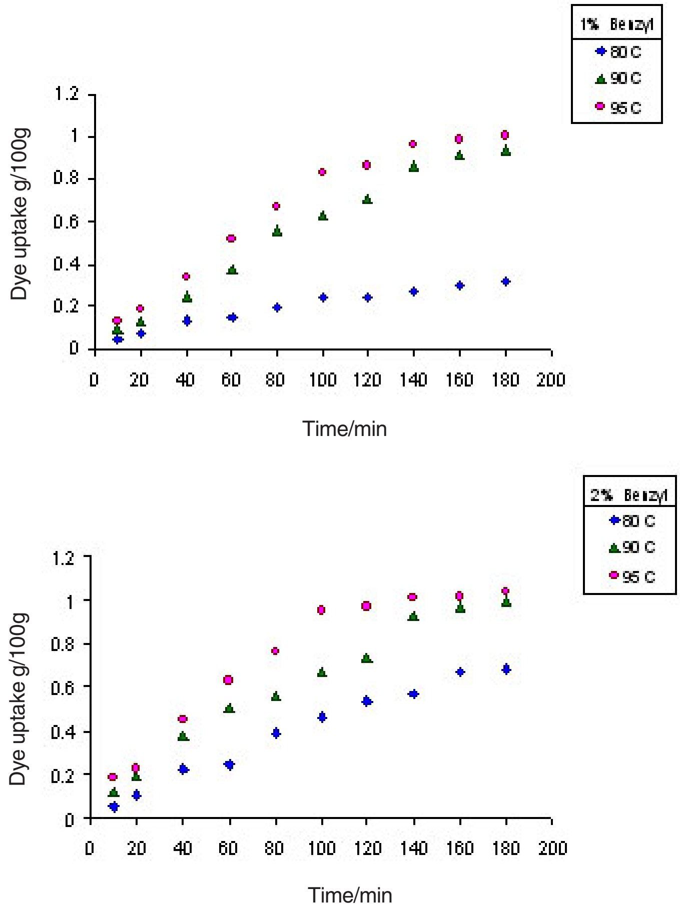


Fig. 2(d): The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Orange 21on Orlon in presence of Benzyl alcohol at different temperatures

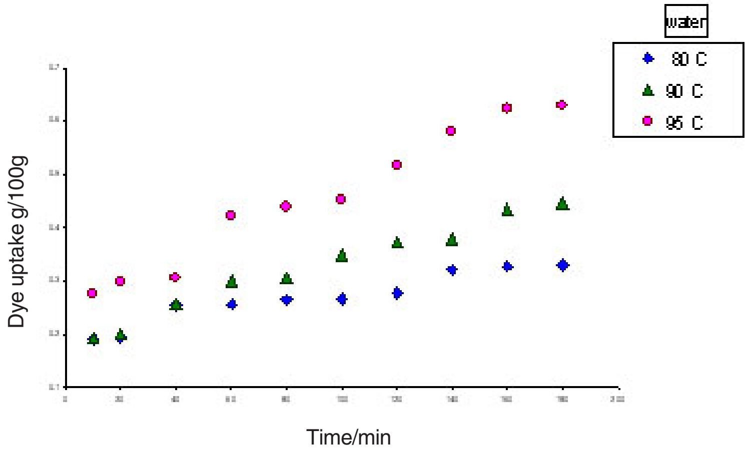


Fig. 2(e) : The Relation between dyeing uptake (g/100 g) and times (min) of C.I. Basic Violet 10 on Orlon in water at different temperatures

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 benzyl alcohol shows no very significant effect on the value of the absorption spectra of the three utilized dyes. The results of Beer s Law was obeyed up to the concentrations investigated. Since the solvent leave the extinction at 2.014×10^4, 3.125×10^4 and $11{,}253\times10^4$L mol^{-1} $cm^{-1}$for C.I. Basic Red12, C.I .Basic 21, and C.I. Basic Violet 10.respectively.

Dyeing in presence of Solvent

The dyeing process can be considered to consist of various stages, migration of dye from solution to the fabric structure as well as the presence of certain chemical groups, which may link up with ionic dyestuff[8]. The addition of certain organic solvents to the dye bath enhances the dye uptake provided these solvents have an effect on fabric. Benzyl alcohol is a comparatively safe solvent to be used in solvent assisted dyeing systems[9]. Table(2) and Fig (2) show that the rate of the dye uptake on the acrylic fabric increases with time, temperature and concentration in absence and presence of benzyl alcohol. In all cases, the results indicated that the uptake of dyes are much more pronounced in presence of 2% (V/V) benzyl alcohol. This was considered as an important factor affecting dyeing process which was acting as a carrier[10]. It is often assumed that the action of carriers causes fabric swelling and this is responsible for easier penetration of the dye in the fibers. Although the addition of benzyl alcohol to the dye bath enhances the dye uptake by opening up the structure of fabric either through lateral swelling or through the

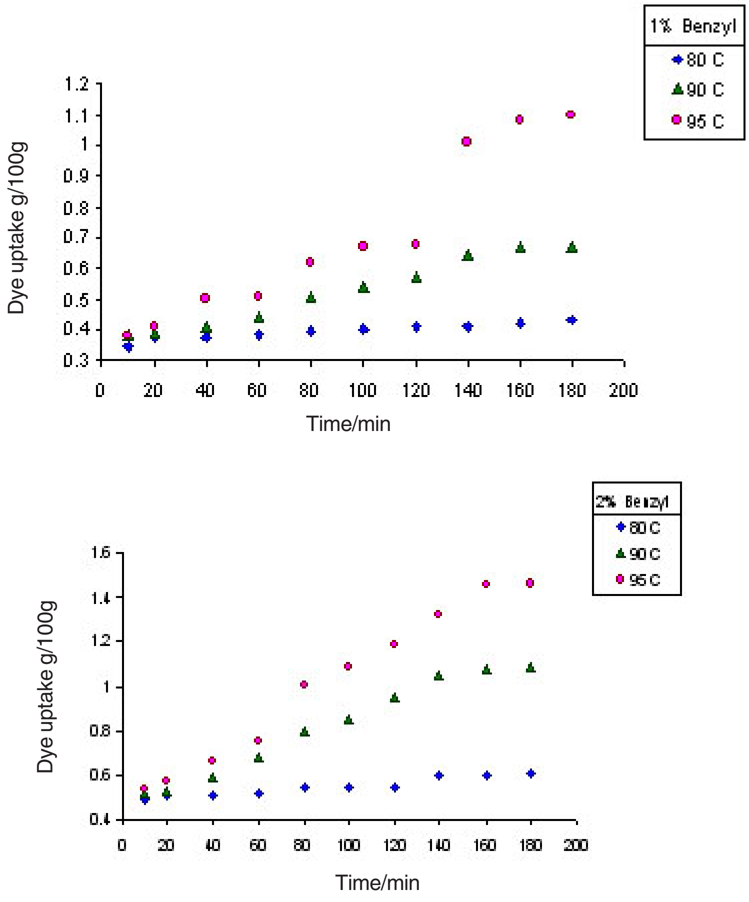


Fig. 2(f) : The Relation between dyeing uptake (g/100 g) and times (min)of C.I. Basic Violet 10 on Orlon in presence of Benzyl alcohol at different temperatures

plasticizing effect, which increase the chain mobility inside the fabric structure[11]. From the data in the Table 2 it can seen that the rate of uptake of the three dyes in presence of benzyl alcohol are greatly increased after 10 minutes. The amount of dye on the acrylic fabric is almost equal to that in absence of alcohol after 180 minutes. In such a case the dye molecules find it relatively easy to approach and be adsorbed on the fiber surface. As the time increases, the dye molecules penetrate the fibers

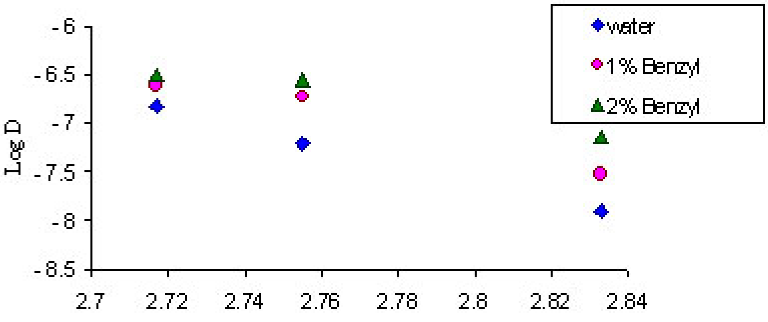


Fig. 3(a): Variation of mean diffusion coefficient with temperatures for C.I. Basic Red 12 in absence and presence solvents

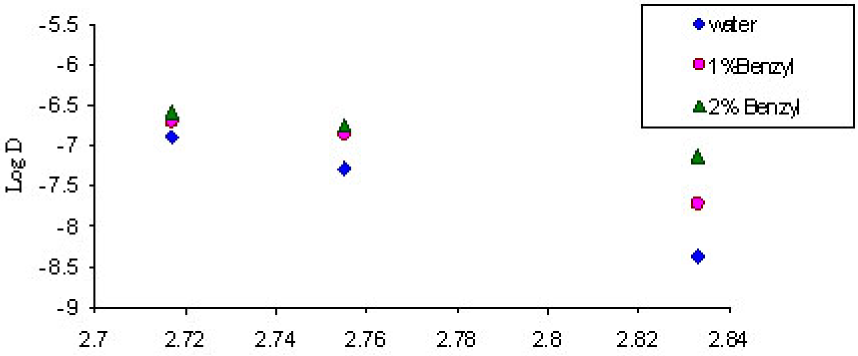


Fig. 3(b): Variation of mean diffusion coefficient with temperatures for C.I. Basic Orange 21in absence and presence solvents

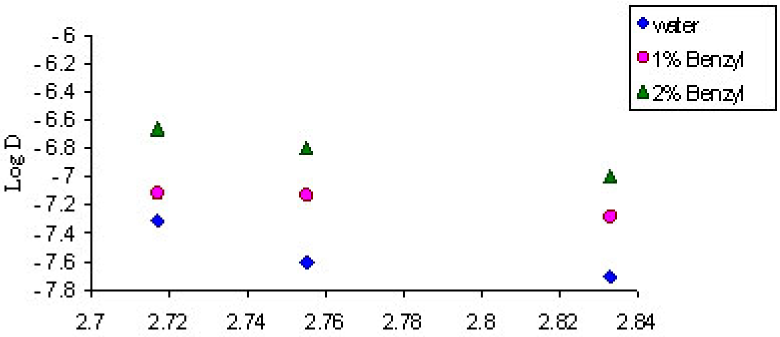


Fig. 3(c) : Variation of mean diffusion coefficient with temperatures for C.I. Basic Violet 10 in absence and presence solvents

and the rate of diffusion of the molecules is also increase[12]. This is clear if we compared the dye uptake for C.I. Basic Red 12 at 80 °C after 2 hours in absence of benzyl alcohol is 0.885 gm/100gm. Fabric but in presence of 2% v/v benzyl alcohol was $2.903x10^2$ gm/100gm fiber. These values increased with increasing temperatures and concentrations of dyes.

Influence of Temperature

Fig. 2 and Table 2 show that the dye uptake of Basic dyes on acrylic increases with increasing time and temperature in absence and presence of solvents. The dye is firstly adsorbed on the surface of the acrylic and then an equilibrium occurs between adsorbed and diffused dye inside the pores. This is clear if we compare the dye uptake at 95 °C in absence and presence of 2%(V/V) benzyl alcohol. It is obvious that there is an increase of the accessibility of the acrylic fabric in the presence of this solvent[1,2]. Showed that the swelling effect of acrylic fabric by benzyl alcohol may be responsible for the increase of dye uptake. The rate of sorption of dye by textile fabrics is controlled by two fundamental physicochemical parameters. At a given dyeing temperature, these parameters include the(i) Penier, Which is proportional to radius of the cylindrical fabric or the apparent radius of the non-cylindrical fabric, and (ii) Liquor ratio[13]. The results indicate in all cases that the dye uptake is higher in presence of solvent than their absence.

The times of half dyeing

The times of half dyeing to 0.5 i.e. the time required for the fiber to uptake half of the amount adsorbed at equilibrium, is often considered as a measure of the rate of adsorption and is given by the Hill equation ;

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

D=apparent diffusion coefficient
r =radius of the fiber
$t_{1/2}$ = time of half dyeing

The determined values $t_{1/2}$ for the tested temperatures are given in Table 3. As can be seen from this table $t_{1/2}$ for these dyes decreased with increasing temperature, and consequently the rate of dyeing increased markedly. Looking for an explanation for such relationships the activation energies and diffusion coefficients for the adsorption process were determined next. For this purpose data for D5 at different temperatures were fitted to an Arrhenius –type equation:

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

D_T=diffusion coefficient at absolute temperature
Do=pre exponential factor (diffusion coefficient for activation energy equal to zero).
Ea= activation Energy
R= Universal gas constant
T= temperature of the process.

Its linear form plotted as log D_T vs 1/T. From the slope of the above fitting, the activation energies (-Ea/2.303R) of the adsorption process of the dye in solution were then estimated in Figs(3a,b,c). These values show that the activation energies are low and hence it can be concluded that the process is governed by interactions of a physical nature. It has been shown by several authors[14-16] that benzyl alcohol acts as plasticizer, reduces glass transition temperature of acrylics under dyeing conditions and therefore can act as dyeing accelerator. In the present work an attempt is made to optimize benzyl alcohol concentration for three basic dyes having different molecular size and to find out possible correlation between optimum benzyl alcohol concentration and molecular size of basic dyes so that a practical solvent assistant dyeing process can be developed for acrylics[9]. The results show

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

The Dyes	Media	λ_{max}	M.wt.g/mol
C.I.Basic Orange 21.	Water Benzyl alcohol	483483	350.89
C.I.Basic Red 12.	Water Benzyl alcohol	485484.6	393.00
C.I.Basic Violet 10	Water Benzyl alcohol	554552.8	479.05

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 x 10^7	Dyeing uptake (k_t) x 10^2										Activation
		cm^2/sec	10 min	20 min	30 min	40 min	50 min	60 min	80 min	120 min	180 min	240 min	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	90	6.118	0.244	0.310	0.925	1.277	1.505	2.584	3.275	4.090	4.209	4.562	Red12
	95	15.020	0.424	0.430	1.836	2.936	3.776	6.319	10.161	13.660	15.877	17.611	
2%Benzyl alcohol	80	7.189	0.829	0.877	1.009	1.268	1.296	1.944	2.539	2.903	3.350	3.629	106.300
in C.I. Basic Red12	90	27.720	0.244	0.310	0.925	1.277	1.505	2.584	3.275	4.090	4.209	4.562	
	95	31.660	1.258	1.790	4.947	9.289	13.885	21.320	28.017	39.772	68.515	81.461	
Water in C.I.	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
Basic Orange21	90	5.173	0.081	0.318	0.617	1.181	1.958	2.264	2.929	6.274	6.848	6.909	
	95	12.730	0.167	0.418	0.763	1.858	4.509	7.190	11.155	19.881	35.881	45.511	
2%Benzyl alcohol in	80	7.354	0.255	0.528	1.302	1.454	2.825	3.766	4.890	5.583	8.272	8.745	90.619
C.I.Basic Orange21.	90	17.720	0.623	1.065	2.686	4.802	5.512	8.310	11.155	35.332	53.920	83.780	
	95	26.090	1.027	1.285	3.559	7.095	12.378	44.025	52.783	115.278	118.945	217.900	
Water in 10	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
C.I.Basic Violet	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	
2%Benzyl alcohol	80	10.047	1.151	1.182	1.200	1.221	1.310	1.328	1.335	1.501	1.525	1.554	29.457
in C.I.Basic Violet 10	90	15.910	1.218	1.276	1.497	1.840	2.475	2.751	3.528	4.470	4.757	4.770	
	95	21.701	1.283	1.428	1.770	2.198	3.957	4.807	6.136	9.012	14.648	15.399	

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
1% Benzyl alcohol	5.141	0.811	0.626
2% Benzyl alcohol	2.103	0.545	0.478
C.I.Basic Orange 21			
Water	35.983	2.923	1.188
1% Benzyl alcohol	7.867	1.069	0.749
2% Benzyl alcohol	2.056	0.853	0.580
C.I.Basic Violet 10			
Water	7.718	6.109	3.096
1% Benzyl alcohol	2.887	2.036	1.971
2% Benzyl alcohol	1.505	0.950	0.697

Table 4: Mean Diffusion Coefficient, Half Time and pH values For Different Dyes in 2% Benzyl alcohol at 95 °C

The Dyes	pH	(D) x 10^7 cm^2/sec.	$t_{1/2}$ min.x10^2
C.I. Basic red 12	2.97	33.049	0.458
	4.45	31.660	0.478
	5.95	27.461	0.551
C.I.Basic Orange21	2.66	28.626	0.528
	3.66	26.060	0.580
	5.89	23.462	0.644
C.I. Basic Violet10	2.62	28.095	0.538
	3.61	21.701	0.697
	5.62	16.599	0.911

that the diffusion coefficient in presence of 2% (V/V) benzyl alcohol 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.

Effects of dyeing on pH

The influence of the pH on the dye uptake at equilibrium for the three dyes examined is shown in Table 4. From the data we can see that the diffusion coefficient of the dye fixed on the fiber decreases as the pH increases. In fact the effect of the pH on the dye uptake is greater with fibers containing only weak acid groups[17-23]. Moreover from Table 4 we can see that C.I. Basic Red 12 has the highest diffusion coefficient .

Eliminate the phrase are observed in studying the kinetics of the process. At this stage, however, it is important to point out that because of the instability of basic dyes, the pH range used in practice is restricted to (2.97-5.95) show how the rate of dyeing increases with increasing pH over this range. This increase is more noticeable with C.I Basic orange21 which contains only weak acidic groups, than with C.I. Basic violet10 which contains both weak and strong acidic groups.

CONCLUSION

The solvents that impart a plasticizing effect on acrylic fibers do improve the dye uptake irrespective of their swelling action on the fibers. The greater the plasticizing effect of the solvent, the more the dye uptake is increased. The obtained results indicate that the dye uptake increases under the different conditions mentioned. The highest dye exhaustion was obtained using 2% (V/V) benzyl alcohol/water mixture this was attributed to the increase in the accessibility of the acrylic fabrics in presence of benzyl alcohol. 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 benzyl alcohol gave another evidence for this conclusion.

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