A Study on the Kinetic and Thermodynamic Parameters of Different Acid Dyes on Nylon 6 Fibers

Amir Shahin Shamsabadi and Mahmoud Feiz

***Abstract*— In this work, the kinetic and thermodynamic parameters of acid dyes on nylon 6 were studied. Acid Sky Blue A, Acid Naphtol Red 6B, and Chrysophenine GX were applied on nylon6 and the dyeing process was conducted at specific conditions. In the early stages of dyeing the linear curve of percentage exhaustion against square root of time was plotted and the ratio of the second root of diffusion coefficient to fiber radius was obtained. Chrysophenine GX with a very high molecular weight, showed the maximum rate of diffusion, and exhaustion, and the lowest time of half-dyeing compared with Acid Sky Blue A and Acid Naphtol Red 6B. Also, adsorption isotherm of the dyes was investigated. The Langmuir type of adsorption was observed for Acid Sky Blue A, while in the case of Acid Naphtol Red 6B and Chrysophenine GX, Freundlich model of adsorption was obtained. The standard affinity of the dyes was calculated from the partition ratio, and Acid Sky Blue A showed the maximum value of standard affinity.**

Keywords: **acid dyes, adsorption isotherm, nylon6, standard affinity, time of half-dyeing**

I. Introduction

The condensation polymerization between diamines and dicarboxylic acids was studied by Carothers in the United States in 1928 for E.I. du Pont de Nemorus and Company Inc., which lead to preparation of one of the most important synthetic fibers [1,2]. These research works led to preparation of a large number of nylon polymers including that produced from Caprolactam which was capable of self-condensation to form nylon 6 [2]. Many patents in the Europe and United States have focused on the technical sides, whereas only the principle of the manufacture of nylon 6 is necessary; the following reaction [3]:

$$\mathrm{HOOC{-}(CH_2)_5{-}NH_2 + HOOC{-}(CH_2)_5{-}NH_2}$$
$$\downarrow$$
$$\mathrm{NH_2(CH_2)_5\,CO\,NH(CH_2)_5\,COOH}$$
$$\downarrow$$
$$\mathrm{H[NH(CH_2)CO]_n\,OH}$$

This reaction proceeds until a long chain is built up leaving an amino group at one end and a carboxyl group at the other [2,3]. Because of these polar groups nylon fibers look like wool fibers and their mechanism of dyeing with acid dyes could be associated with amino end groups in the fiber. Also the adsorption of acid dyes on nylon depends on pH of the dyebath [4-7]. In the dyeing of nylon fibers with acid dyes, ionic links are formed due to the attraction between positive and negative charges; therefore positive charge amino groups ($-NH_3^+$) in nylon attract the anions of acid dyes and consequently the acid dyes are adsorbed on to the fibers [7-9]. Van der Waals forces can affect the adsorption and the strength of the attraction is proportional to the area of possible contact between dye molecules and fibers which depends on the structure of the dye. Thus, large, flat and high molecular weight dye molecules would be firmly held by fiber [9,10].

Dyeing takes place in three stages; 1- transfer of dye from solution to the surface of the fiber, 2- adsorption of dye at the fiber surface and 3-diffusion of dye from surface to inner parts of the fiber [10,11]. Diffusion of dye into the fiber is governed by Fick's law:

$$\frac{ds}{dt} = -D\frac{dc}{dx} \tag{1}$$

where ds is the amount of dye diffusing across unit area in a very small interval of time dt, c is the concentration at a point x, the distance diffused, and D is the diffusion coefficient [10,11]. In the above form, Fick's equation is not well adjusted to the experimental results [10].

In the early stages of exhaustion, with a cylindrical fiber of radius r, and with ordinary dyeing at a given temperature, according to the following simple approximate relationship, if C_t/C_∞ or percentage exhaustion is plotted against the square root of the time, a straight line would be obtained and $\sqrt{D}/r$ can be obtained from the slope of this line [10]:

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{Dt}{\pi r^2}} \tag{2}$$

Also the time of half-dyeing is an indirect measurement of the rate of diffusion in the fiber. If dyeing is carried out at a given temperature and the exhaustion at different times is plotted against time of dyeing, the exhaustion curve is obtained and therefore the time to attain half the final equilibrium can be measured. The time of half-dyeing ($t_{1/2}$) is inversely proportional to the rate of diffusion in the fibers; a low value of time of half-dyeing shows rapid diffusion and vice versa [10].

Adsorption isotherms can be expressed graphically after conducting dyeing to equilibrium at a fixed temperature with different amounts of dye, and then measuring the

A. Sh. Shamsabadi and M. Feiz are with the Department of Textile Engineering, Isfahan University of Technology, Isfahan, Iran. Correspondence should be addressed to M. Feiz (e-mail: m_feiz@cc.iut.ac.ir).

amount of dye on the fiber $[D]_\theta$, and in the residual dyebath $[D]_\sigma$ [8-10]. Due to ion-exchange mechanism, the uptake of acid dye by nylon can be described in terms of Langmuir adsorption isotherm, in which the dye anion molecules taken up by the polymer molecules are attached to the positively charged amino groups. At the same time, the adsorption can be accompanied by an excess dye sorption, i.e., the amount of adsorbed dyes exceeds the equivalent amino group content of the nylon [8,9,13,14]. Also to describe the relation between the amount of acid dye adsorbed on nylon6 and the amount of dye in the residual dyebath, some other types of adsorption isotherm like Freundlich, Dubinin-Radushkevichand, Redlich-Peterson, and dual-mode sorption models were used [8,9,15].

As the dyeing process reaches true equilibrium state, the adsorption and desorption of dye on the fiber can take place at the same rate. The chemical potential of the dye in the fiber and that in the solution, under these conditions can be the same and there is no net transfer of dye from one phase to the other. Also, due to higher affinity of the dye for the fiber than for the water, the concentration of dye in both phases are not equal [4,10,11]. The standard affinity $(-\Delta\mu^\circ)$ is calculated by using the following equation:

$$-\Delta\mu^\circ = RT \ln k \quad (3)$$

where, R is the gas constant, T is the absolute temperature, and k is the partition ratio [4,9,11].

For investigation of dyeing behavior of acid dyes on nylon, these dyes can be categorized into three sub groups. Group 1: dyes with little affinity for nylon; group 2: dyes with moderate affinity for nylon which form the largest group; and group 3: dyes which exhibit a high affinity for nylon [2].

The aim of this research work is to investigate the kinetic and thermodynamic parameters of three acid dyes from different groups on nylon 6 fibers. In the first approach, diffusion coefficient and time of half-dyeing from exhaustion curves were obtained. Also the adsorption isotherms of the dyes on the fiber were investigated and standard affinity of the acid dyes for nylon 6 fibers was calculated.

II. Experimental

A. Materials and Instruments

Nylon 6 fibers were purchased from Tehran Aliaf Public Joint Stock CO. Prior to dyeing the fibers were wetted out in cold tap water.

The following commercial dyes were used (three different acid dyes belonging to different groups): Acid Sky Blue A (C.I. Acid Blue 5, from HebeiYouhao Chemical Co., Ltd), Acid Naphtol Red 6B (C.I. Acid Violet 7, from Jinan Haohua Industry Co., Ltd) and Chrysophenine GX (C.I. Direct Yellow 12, from Kaseihin Kogyo Kyokai).

Formic acid, acetic acid, and ammonium acetate were purchased from Merck Chemical Co and Sigma-Aldrich (a part of Merck).

Absorbance measurements were carried out using a UV-240 (Shimadzu Co., Japan) UV-visible spectrophotometer. Dyeing was conducted in Ahiba-Polymat and Ahiba-Turbomat Laboratory scale dyeing machines (Ahiba1000, Datacolor Co., Switzerland).

B. Absorbance Test

To obtain the wavelength of maximum absorbance (λ_{max}), a dye solution of each dye with a concentration of 10 mg L^{-1} was prepared. Absorbance spectra of solutions were determined using UV-240 spectrophotometer over the range of 380 to 720 nm. The wavelength of maximum absorbance of the dyes, as an important dye characteristic, was measured to be 400, 520 and 634 nm for Chrysophenine GX, Acid Naphtol Red 6B and Acid Sky Blue A, respectively.

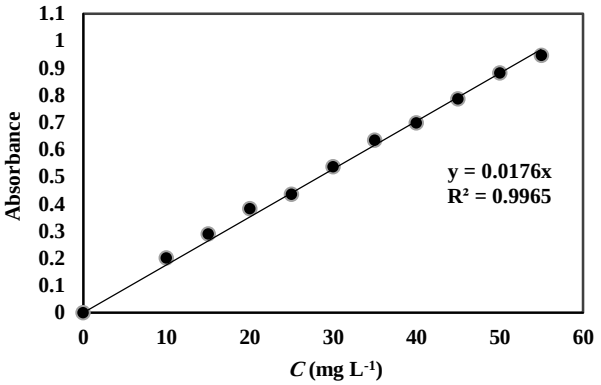

Fig. 1. Calibration curve for Acid Sky Blue A (at λ_{max}= 634 nm).

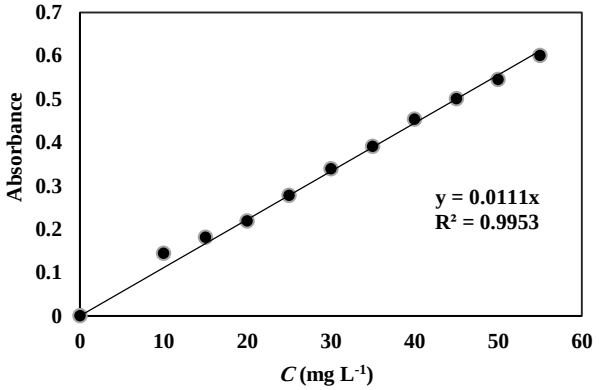

Fig. 2. Calibration curve for Acid Naphtol Red 6B (at λ_{max}= 520 nm).

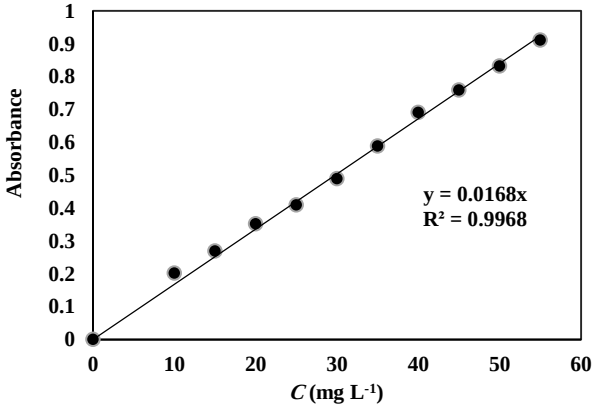

Fig. 3. Calibration curve for Chrysophenine GX (at λ_{max}= 400 nm).

C. Calibration Curve

To have a calibration curve, ten dye solutions with different concentrations were prepared. The absorbance of the solutions was measured by using the UV-visible spectrophotometer at the wavelength of maximum absorbance of each dye (i. e., 400, 520, and 634 nm for Chrysophenine GX, Acid Naphtol Red 6B And Acid Sky Blue A, respectively), and the calibration curve was obtained (Figs. 1 to3).

D. Exhaustion Curves

All dyeings in this step of work were carried out using fibers (5 g) which had been wetted out in tap water, in stainless steel dye pots housed in Ahiba-Turbomat laboratory scale dyeing machine using a 1% on weight of fiber (o.w.f) of dye, and a liquor ratio of 50:1. The dyeing procedure is shown in Fig. 4, according to the recommended method for each dye [12].

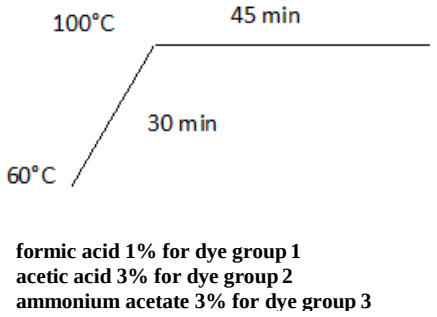

Fig. 4. Dyeing method.

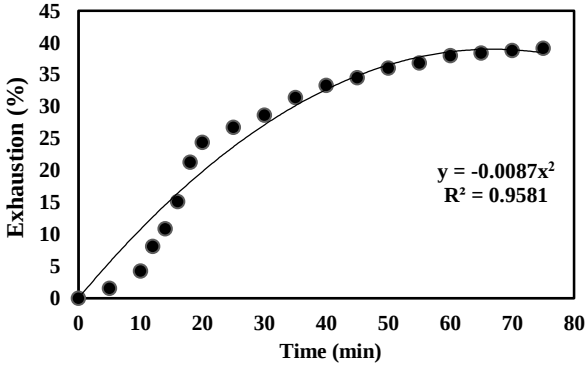

Fig. 5. Exhaustion curve for Acid Sky Blue A on nylon 6.

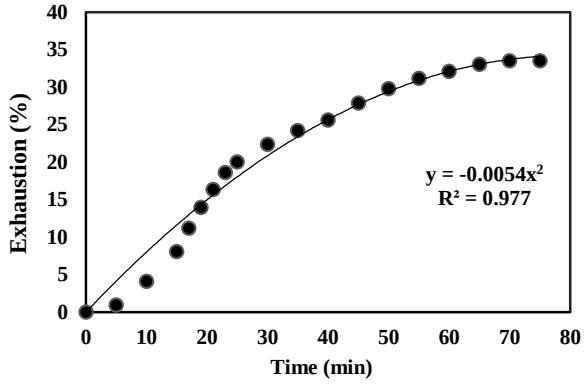

Fig. 6. Exhaustion curve for Acid Naphtol Red 6B on nylon 6.

Samples were taken from the dyebath every five minutes (in the critical point every two minutes) during the dyeing. The amount of dye remained in the dyebath at any time of the dyeing process was obtained by using absorbance values which were measured by UV-visible spectrophotometer at the wavelength of maximum absorbance of the dyes (i. e., 400, 520, and 634 nm for Chrysophenine GX, Acid Naphtol Red 6B And Acid Sky Blue A, respectively) and the calibration curves. Therefore the exhaustion curves were obtained (Figs. 5 to 7).

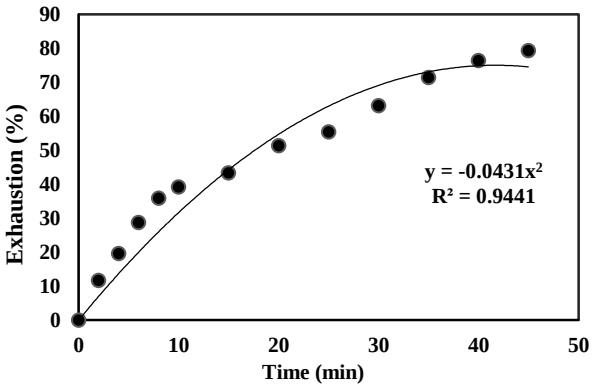

Fig. 7. Exhaustion curve for Chrysophenine GX on nylon 6.

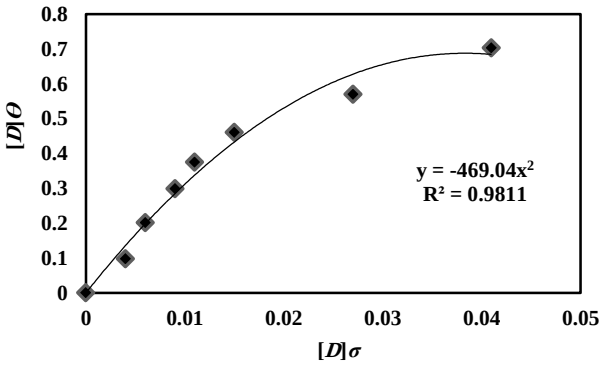

Fig. 8. Adsorption isotherm for Acid Sky Blue A on nylon 6.

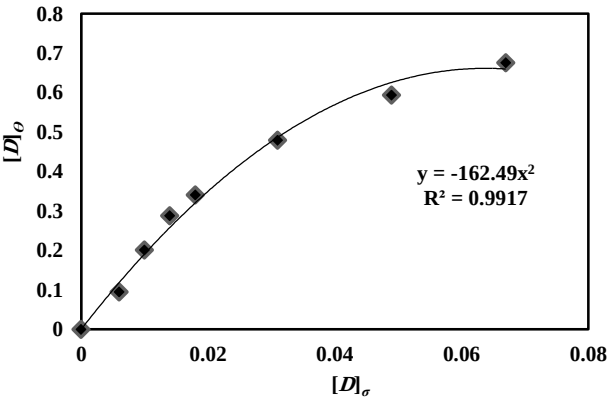

Fig. 9. Adsorption isotherm for Acid Naphtol Red 6B on nylon 6.

E. Adsorption Isotherms

To obtain Adsorption isotherms, previously wetted nylon 6 fibers (2.5 g) were sealed in stainless steel dye pots of 100 mL capacity housed in a Ahiba-Polymat laboratory scale dyeing machine, using dye solutions with seven

different concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g L^{-1}, and a liquor ratio of 50:1, for 90 min at 100 °C. When dyeing was finished, the amount of dye remained in the dyebath was obtained by using the absorbance measured at the wavelength of maximum absorbance of the dyes (i. e., 400, 520, and 634 nm for Chrysophenine GX, Acid Naphtol Red 6B and Acid Sky Blue A, respectively) and the calibration curve. The adsorption isotherms are shown in Figs. 8 to 10. The amount of the dye adsorbed on the fibers was calculated by subtracting the dye amount remaining in the dyebath from the initial dye amount.

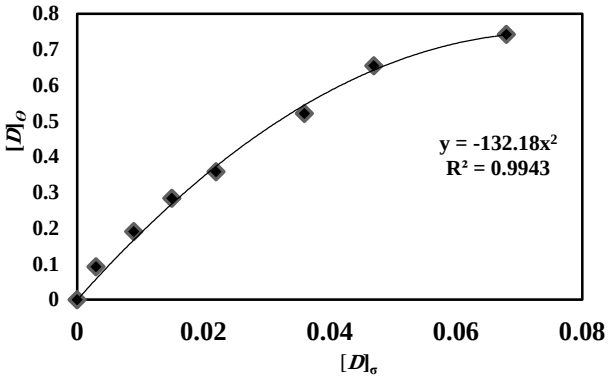

Fig. 10. Adsorption isotherm for Chrysophenine GX on nylon 6.

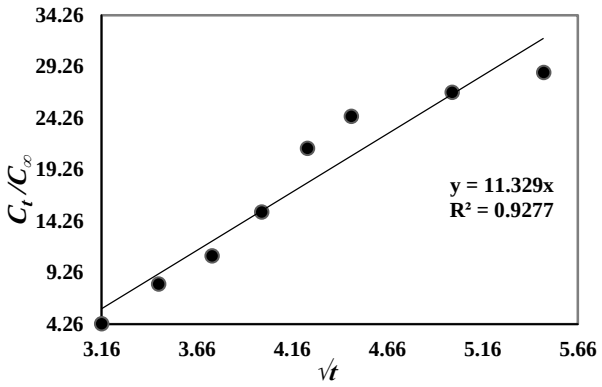

Fig. 11. C_t/C_∞ vs. $\sqrt{t}$ for Acid Sky Blue A on nylon 6.

III. Results and Discussion

In this work the rate of diffusion and exhaustion of three different acid dyes (Acid Sky Blue A belongs to group 1, Acid Naphtol Red 6B belongs to group 2 and Chrysophenine GX belongs to group 3) on nylon 6 fibers was examined. In the first approach the exhaustion curves were obtained. Then, in the early stages of dyeing the percentage exhaustion versus the square root of the time was plotted in which the slope of the straight line was proportional to $\sqrt{D}/r$ (Figs.11 to 13).

It can be seen from Table I that the exhaustion and diffusion rate of Acid Sky Blue A, is more than Acid Naphtol Red 6B, and the result obtained from this work is compatible with other's work [10]. But in the case of Chrysophenine GX (which is generally used as a direct dye) with a very high molecular weight, when used at pH 6 on nylon, the highest exhaustion and diffusion rate compared with Acid Sky Blue A and Acid Naphtol Red 6B was observed.

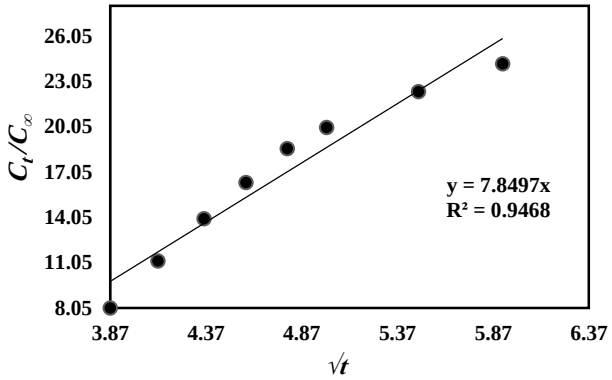

Fig. 12. C_t/C_∞ vs. $\sqrt{t}$ for Acid Naphtol Red 6B on nylon 6.

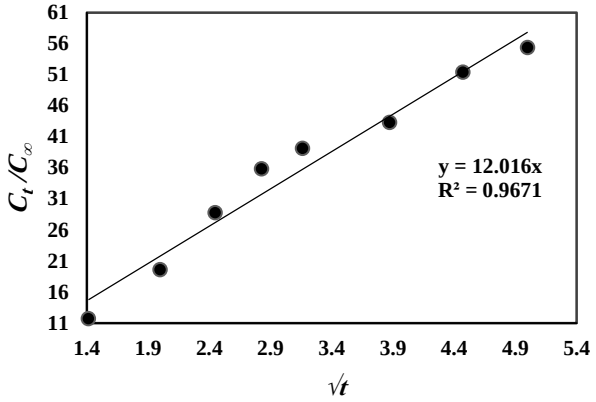

Fig. 13. C_t/C_∞ vs. $\sqrt{t}$ for Chrysophenine GX on nylon 6.

Acid Sky Blue A, which belongs to group 1 of acid dyes with low van der Waals forces has more diffusion rate than Acid Naphtol Red 6B and Chrysophenine GX which has a very high molecular weight and attach to nylon molecules through van der Waals forces and ionic links ($-NH_3^+D^-$). So it can be seen that Chrysophenine GX molecules diffuse more rapidly to the fibers than other acid dyes used in this work. Also, the time of half-dyeing for Acid Sky Blue A, Acid Naphtol Red 6B, and Chrysophenine GX on nylon 6

TABLE I
Acid Dyes Properties

name of dye	traditional name	molecular weight (g mol^{-1})	$\frac{\sqrt{D}}{r}$	$t_{1/2}$ (min)	k	$\Delta\mu^\circ$ (kJ mol^{-1})
C.I. Acid Blue 5	Acid Sky Blue A	631	1.60	17.4	31.93	10.73
C.I. Acid Violet 7	Acid Naphtol Red 6B	522	1.11	21.3	17.07	8.83
C.I. Direct Yellow 12	Chrysophenine GX	680	1.69	8.8	15.70	8.53

fibers was obtained. Table I shows that Acid Sky Blue A hada more exhaustion rate compared with Acid Naphtol Red 6B, and the most exhaustion rate was observed for Chrysophenine GX.

To have an economical dyeing process, the dyebath should be well exhausted and the final concentration of dye on fiber at equilibrium must be at very high percentage of exhaustion. Adsorption isotherms provide useful information on the dyeing mechanism. Three types of adsorption isotherms referred to as Nernst, Eq. (4); Langmuir, Eq. (5); and Freundlich, Eq. (6) [9,10] were considered in the dyeing processes. The Nernst adsorption isotherm describes the distribution of a solute between two immiscible solvents and is linear up to the point corresponding to the dye saturation on the fiber.

$$\left[D\right]_{\theta} = K\left[D\right]_{\sigma} \tag{4}$$

The Nernst adsorption isotherm was not considered in this work. Figs. 8 to 10 show that the results obtained from the equilibrium adsorption of Acid Sky Blue A, Acid Naphtol Red 6B and Chrysophenine GX on nylon fibers were fitted well by Langmuir and Freundlich adsorption isotherms, i.e. Eqs. (5) and (6), respectively.

As can be seen in Fig.8 the adsorption isotherm of Acid Sky Blue A on nylon 6 shows a Langmuir type of adsorption which implies the presence of a definite number of sites on which adsorption can take place by ionic links. Consequently $[D]_{\theta}$ reaches a maximum.

$$\left[D\right]_{\theta} = \frac{K\left[S\right]_{\theta}\left[D\right]_{\sigma}}{1 + K\left[D\right]_{\sigma}} \tag{5}$$

Where K is a constant and $[S]_{\theta}$ is the concentration of dye on the fiber when all the sites are occupied.

In the case of Chrysophenine GX and Acid Naphtol Red 6B the Freundlich adsorption model was observed, possibly due to the relatively high molecular weight of the dyes which can increase van der Waals forces between dye molecules and the fiber (Figs. 9 and 10).

$$\left[D\right]_{\theta} = K\left[D\right]_{\sigma}^{x} \tag{6}$$

Also the values of partition ratio (k) and standard affinity ($\Delta\mu^{\circ}$) were obtained and are presented in Table I. The values of standard affinity are negative; confirming that the adsorption of acid dyes on to nylon 6 fibers is spontaneous and thermodynamically favorable. The more negative values of $\Delta\mu^{\circ}$ imply a greater driving force to the adsorption process.

It can be seen from Table I that the maximum standard affinity and partition ratio was observed for Acid Sky Blue A, and Acid Naphtol Red 6B had more standard affinity than Chrysophenine GX.

In the case of Acid Sky Blue A which was applied at lower pH, the dye anions attached to the nylon through the strong ionic linkage ($-NH_3^+D^-$) in addition to van der Waals forces, whereas for Chrysophenine GX which was used at a weak acidic condition (pH 6), the dye molecules adsorbed on to the nylon fibers mostly through van der Waals forces. Therefore, Acid Sky Blue A had the most standard affinity; and Acid Naphtol Red 6B had much more affinity than Chrysophenine GX.

IV. Conclusion

Three different dyes from different classes of acid dyes were applied on nylon 6 fibers and their dyeing behaviors were investigated. The dyeing was carried out for each dye under given conditions and the exhaustion curves were plotted. In the early stages of dyeing, percentage exhaustion was plotted against square root of time and from the slope of the curves, $\sqrt{D}/r$ was obtained; also time of half-dyeing was calculated for each dye. The results showed that Chrysophenine GX with a very high molecular weight had the most exhaustion and diffusion rate, whereas Acid Sky Blue A which belongs to group 1, diffused more rapidly to the fibers than Acid Naphtol Red 6B.

The adsorption isotherm of Acid Sky Blue A followed Langmuir adsorption model whereas for Chrysophenine GX and Acid Naphtol Red 6B, Freundlich type of adsorption isotherm was observed.

It can be concluded that the partition ratio and standard affinity decrease from dye group 1 to dye group 3 due to the increase in pH. As the pH increases, the $\Delta\mu^{\circ}$ values decrease, indicating less driving force (ionic links), resulting in lesser adsorption capacity.

Acknowledgment

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References

[1] V. B. Gupta and V. K. Kothari, “Nylon 6 and nylon 66 fibers”, in *Manufactured fiber technology*, 1st ed., London: Chapman and Hall, 1997, pp. 318-356.

[2] D. M. Nunn, “Dyeing of nylon and polyurethane fibers”, in *Dyeing of synthetic-polymer and acetate fibers*, Yorkshire: DC Publications Trust, 1979, pp. 241-340.

[3] R.H. Peters, “Nylon fibre: A study of the mechanism of the dyeing Process with acid dyes”, *Color. Technol*., vol. 61, no. 4, pp. 85–103, 1945.

[4] R. H. Peters, “The adsorption of acids and acid dyes by nylon”, in *Textile Chemistry*, vol. 3, Amsterdam: Elsevier scientific publishing company, 1974, pp. 295-343.

[5] E. Atherton, D. A. Downey, and R. H. Peters, “Some observations on the dyeing of nylon with mixtures of acid dyes”, *Color. Technol*., vol. 74, no. 4, pp. 242-251, 1958.

[6] E. R. Trotman, “Synthetic fibers”, in *Dyeing and chemical technology of textile fibers*, 4th ed., London: Charles Griffin & Co. Ltd, 1970, pp. 131-160.

[7] E. Atherton, D. A. Downey, and R. H. Peters, “Studies of the dyeing of nylon with acid dyes—Part I: Measurement of affinity and the mechanism of dyeing”, *Text. Res. J.*, vol. 25, no. 12, pp. 977-993, 1955.

[8] M. Safi, “Study of dyeing behavior of nylon 6 fibers with acid dyes”, *J. ColorSci. Technol.*, no. 2, pp. 95-103, 2011.

[9] H. A. Tayebi, M. A. Yazdanshenas, A. Rashidi, R. Khajavi, and M. Montazer, “The Isotherms, Kinetics, and Thermodynamics of Acid Dye on Nylon6 with Different Amounts of Titania and Fiber Cross Sectional Shape”, *J. Eng. Fiber. Fabr.*, vol. 10, no. 1, pp. 97-107, 2015.

[10] C. L. Bird, "The theory of wool dyeing", in *Theory and practice of wool dyeing*, 4th ed., Yorkshire: SDC, 1972, pp. 7-46.
[11] A. D. Broadbent, "Dyeing theory", in *Basic principles of textile coloration*, Yorkshire: SDC, 2001, pp. 197-215.
[12] C. H. Giles, "Anionic dyes", in *A Labratoary course in dyeing*, Yorkshire: SDC, 1974, pp. 98-101.
[13] T. Tak, J. Komiyama, and T. Iijima, "Dual sorption and diffusion of acid dyes in nylon", *Sen'igakkaishi*, vol. 35, no. 11, pp. 96-101, 1979.
[14] P. Viallierand C. Jordan, "Nylon 6.6 dyeing behaviour for fibres of different levels of fineness", *Color. Technol.*, vol. 117, no. 1, pp. 30-34, 2001.
[15] T. Shibusawa, "Sorption of azo disperse dyes by nylon 6 from water",*Text. Res. J.*, vol. 66, no. 1, pp. 37-44, 1996.