

Interaction of Dyes Used for Foods with Food Packaging Polyamides

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SYNOPSIS

The effect of pH, temperature, dye concentration, and additives on the adsorption of the dyes FD & C (Food, Drugs & Cosmetics) Blue 1 and Blue 2 upon the polyamides nylon 4–7, 9, and 10–12 was studied and a correlation between these parameters and the dye uptake was found. The adsorption kinetics of the dyes on the polyamides were studied and a mechanism based on the interaction of the acid groups of the dyes and the positively charged groups of the polyamides was suggested. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The importance of the appearance of a food product with regard to its acceptance and further promotion by the consumer is well known and its color is a characteristic of major significance that defines the appearance of the product.

Natural dyes including those obtained *in vitro* by plant tissue culture or by chemical synthesis have been increasingly used recently for coloring food-stuffs, but synthetic dyes are still used predominantly, because of their higher extinction coefficients, stability, and lower price.^{1,2} These dyes are primarily used in highly processed foods such as soft drinks and baked goods.³

On the other hand, in the last 15 years, there has been a large increase in the use of plastic materials for food packaging. Plastics, once perceived as inconsiderable by food processors and consumers, are now often seen as the best form of available packaging material.^{4,5} Among them, polyamides are ex-

tensively used because of their excellent gas barrier properties in conjunction with their satisfactory mechanical properties (high Young's modulus and elongation).^{6–11}

Synthetic dyes used in the food, drug, and cosmetic industries are low molecular weight acid dyes containing sulfonic groups in their molecules. However, the utilization of synthetic dyes as food additives has some undesirable consequences such as bleeding of dyes between food components or migration into the packaging material and, also, problems caused by interactions between food colorants and packaging material that result in an unappetizing and unsanitary looking product. Thus, the packaging industry is currently investigating how specific packaging materials interact with foods. Interactions between the amine or amide groups of the polyamide chain and the sulfonic groups of the dye molecules were previously reported,^{1,12} but the existing literature in this field is limited.

Melt spinning is widely used in industrial production of fibers. Previous publications have shown that at very high spinning speeds (over 3000 mpm) polyamides contained a large proportion of well-ordered and large crystals. The crystallinity at high take-up velocity (3000 mpm) decreases with increasing molecular weight, whereas at low take-up

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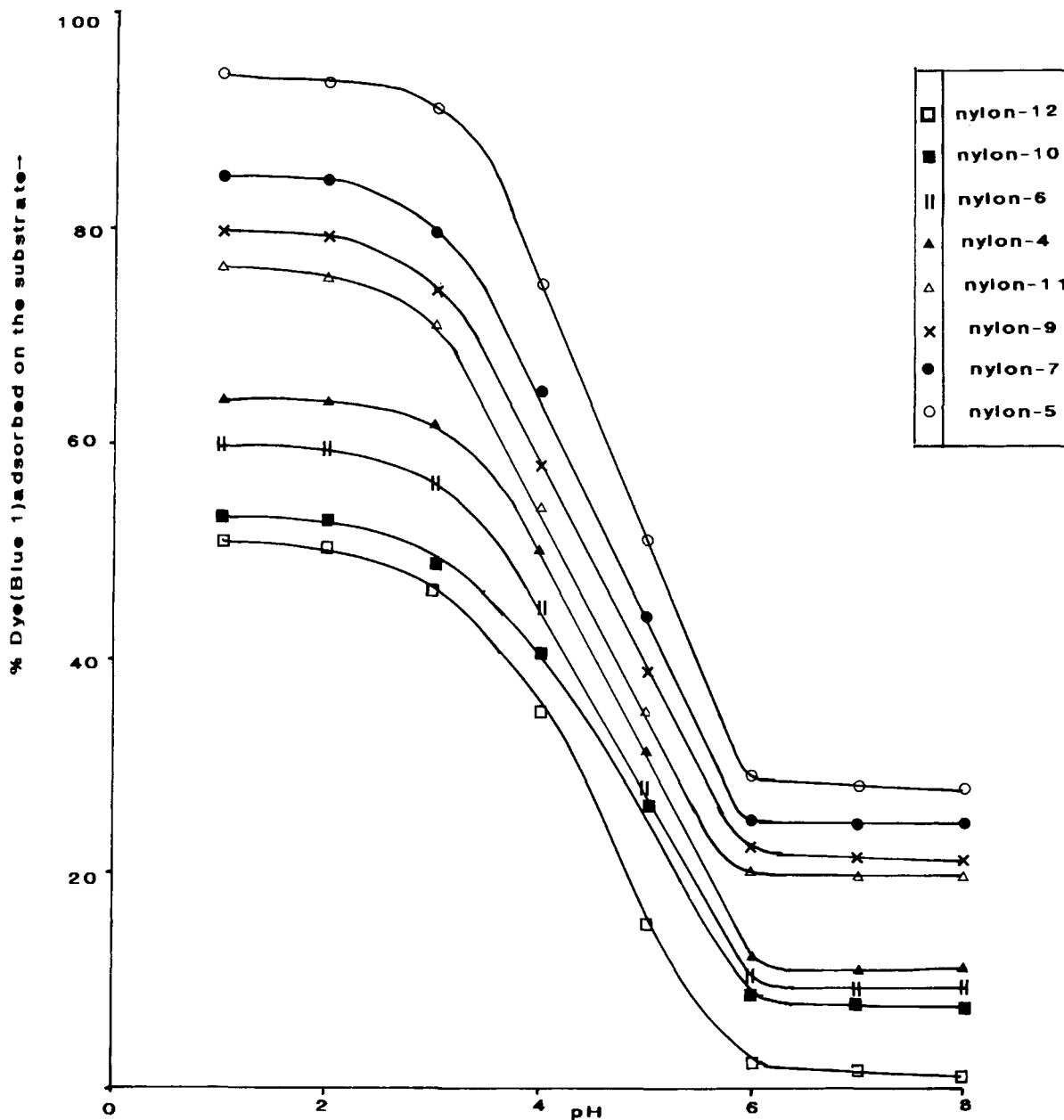


Figure 1 Effect of the pH on the adsorption of Blue 1 on different polyamides at 23°C after 2 h (exposure time).

velocity (1000 mpm), the opposite trend was observed.¹³⁻¹⁸

The amorphous as-spun nylon fibers can develop orientation by either hot or cold drawing, although cold drawing of as-spun nylon fibers induces a growth in the crystalline orientation of both and phases did not occur until the draw ratio is about three.¹⁹⁻²¹ The oriented fiber is visualized as a mass of nearly parallel, fibrous molecules that are occa-

sionally in perfect alignment and in gradually descending order of regularity to some degree of randomness. It was suggested that the strength of the fiber largely depends on the length of the molecules joining the strong crystalline regions to each other since the amorphous regions would have only a low strength.²²

This work was undertaken to provide a better understanding of the mechanism and the conditions

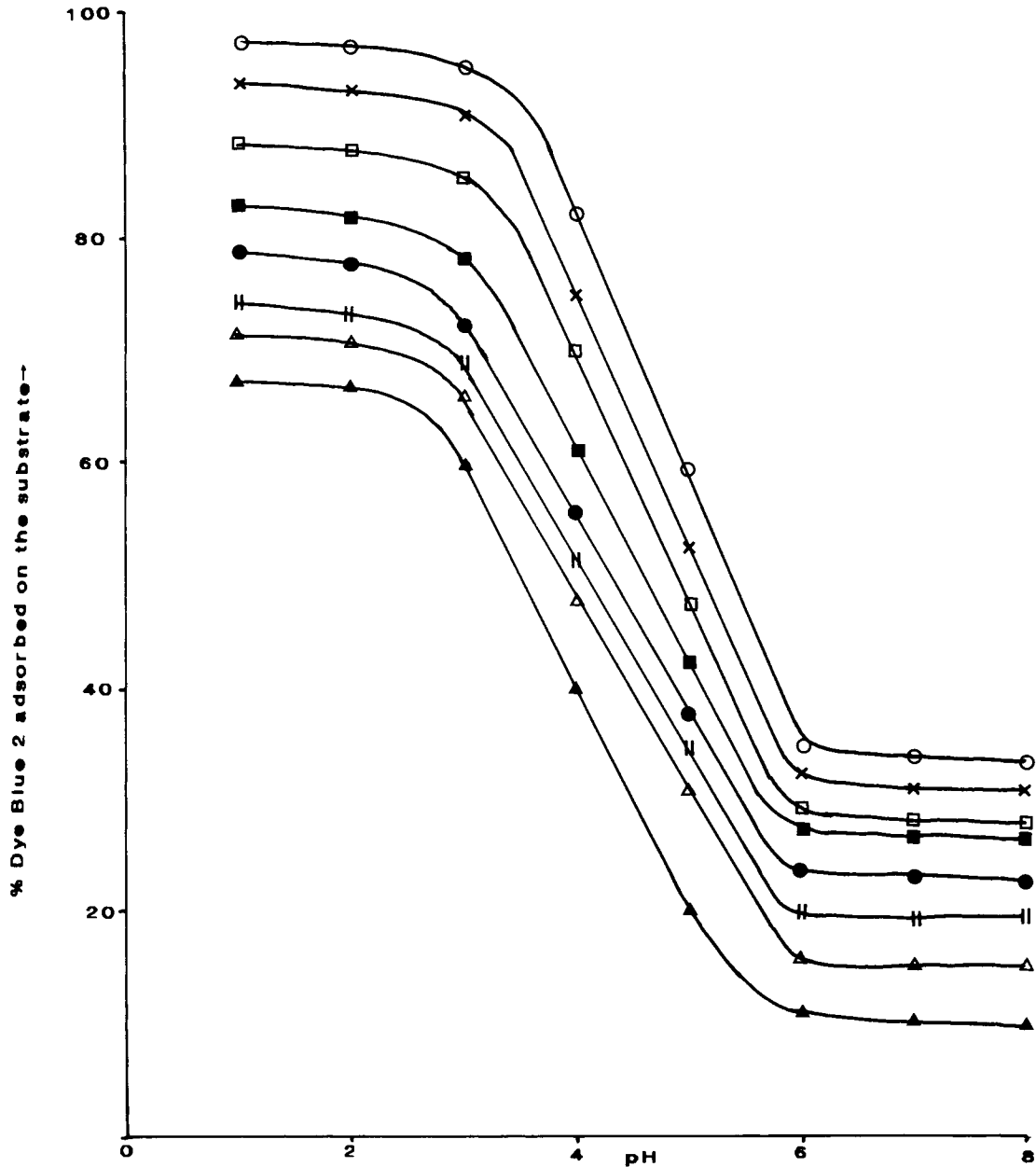


Figure 2 Effect of the pH on the adsorption of Blue 2 on different polyamides at 23°C after 2 h (exposure time). For symbols, see Figure 1.

under which this dye migration from food to polyamide packaging takes place. The influence of pH value, temperature, dye concentration, and additives on the dye adsorption by the polyamides was investigated and the adsorption kinetics at different temperatures and at pH 3 were studied. A mechanism based on the correlation between structural features of the dye and the polymer substrate and the dye sorption was suggested.

2. EXPERIMENTAL

2.1. Materials

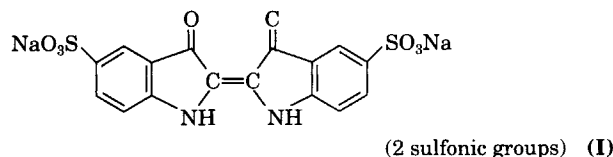
2.1.1. Polyamides

Polyamide fibers were prepared by melt extrusion at a spinning speed of 2500 mpm. Nylon as-spun fibers were subsequently cold drawn at a moderate draw ratio (draw ratio = 2).

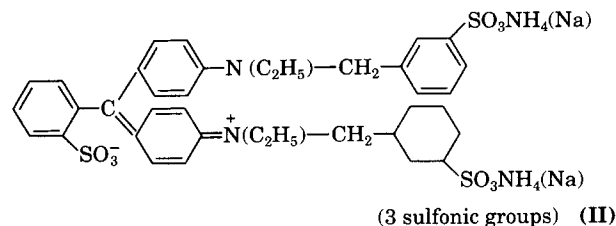
2.1.2. Dyes

Dyes were purchased from commercial companies in the powder form as their sodium salts (Warner Jenkinson, St. Louis, MO). Stock solutions were prepared in distilled water at concentrations of 1000 ppm. Visible spectrometry was used for checking the solutions against possible degradation. The following two dyes were used:

(a) C.I. Food Blue 1 73015²³:



(b) C.I. Food Blue 2 42090²³



2.1.3. Substrates

The substrates consisted of standard 5 g samples of the polyamide fibers that were exposed to solutions

of the dyes using an Ahiba WBRG 60 Texomat (Ahiba, Charlotte, NC). The polyamides were purchased from Ciba-Geigy and could be classified in odd and even numbers (i.e., nylons 5, 7, 9, and 11 and 4, 6, 10, and 12, respectively).

2.2. pH Variation

Solutions of the dyes, 20 ppm, were prepared by diluting the initially prepared stock solution of 1000 ppm dye. This particular concentration (20 ppm) of the dye was chosen because it is the one used on a commercial scale for the production of instant beverages. The pH of the solutions was adjusted to 1 unit increments within a range from 2 to 8 because this is the pH range of most foodstuffs.¹ The pH adjustments were made using 1.0M citric acid or sodium hydroxide solutions. Substrates were exposed to the solutions for a period of 2 h under controlled temperatures ($23 \pm 2^\circ\text{C}$).

2.3. Concentration Variation

The range of concentrations used was 10–60 ppm. Six concentrations (10, 20, 30, 40, 50, and 60 ppm) of the dye solution were used in total. These concentrations were chosen because they are most commonly used in beverage drinks.¹ The solutions were adjusted to pH 3 with 1.0M citric acid. Exposure time and temperature of these substrates to the above-mentioned six solutions were 2 h and 23°C , respectively.

Table I Average Amino End Groups,^a Carboxylic End Groups,^b and Percentage Crystallinity^c (% K) and Glass Transition Temperatures^d (T_g , K) of Polyamide Samples

		Amino End Groups, e.g., —NH ₂ / <i>M_n</i>	Carboxylic End Groups, e.g., —COOH/ <i>M_n</i>	% K	<i>T_g</i> (K)
Odd-numbered polyamides	Nylon 5	1.24	0.83	30.4	318.6
	Nylon 7	1.19	0.71	33.0	325.2
	Nylon 9	1.12	0.65	32.5	319.4
	Nylon 11	1.06	0.60	36.0	316.1
Even-numbered polyamides	Nylon 4	0.95	0.56	34.2	353.0
	Nylon 6	0.79	0.48	37.0	325.2
	Nylon 10	0.70	0.40	36.0	315.3
	Nylon 12	0.61	0.35	30.9	314.8

^a Determined from titration and UV spectroscopy methods.³⁶

^b Determined by the Waltz and Taylor method.³⁷

^c Determined from DSC³⁸ and X-ray diffraction patterns.³⁸

^d Determined from DSC.³⁸

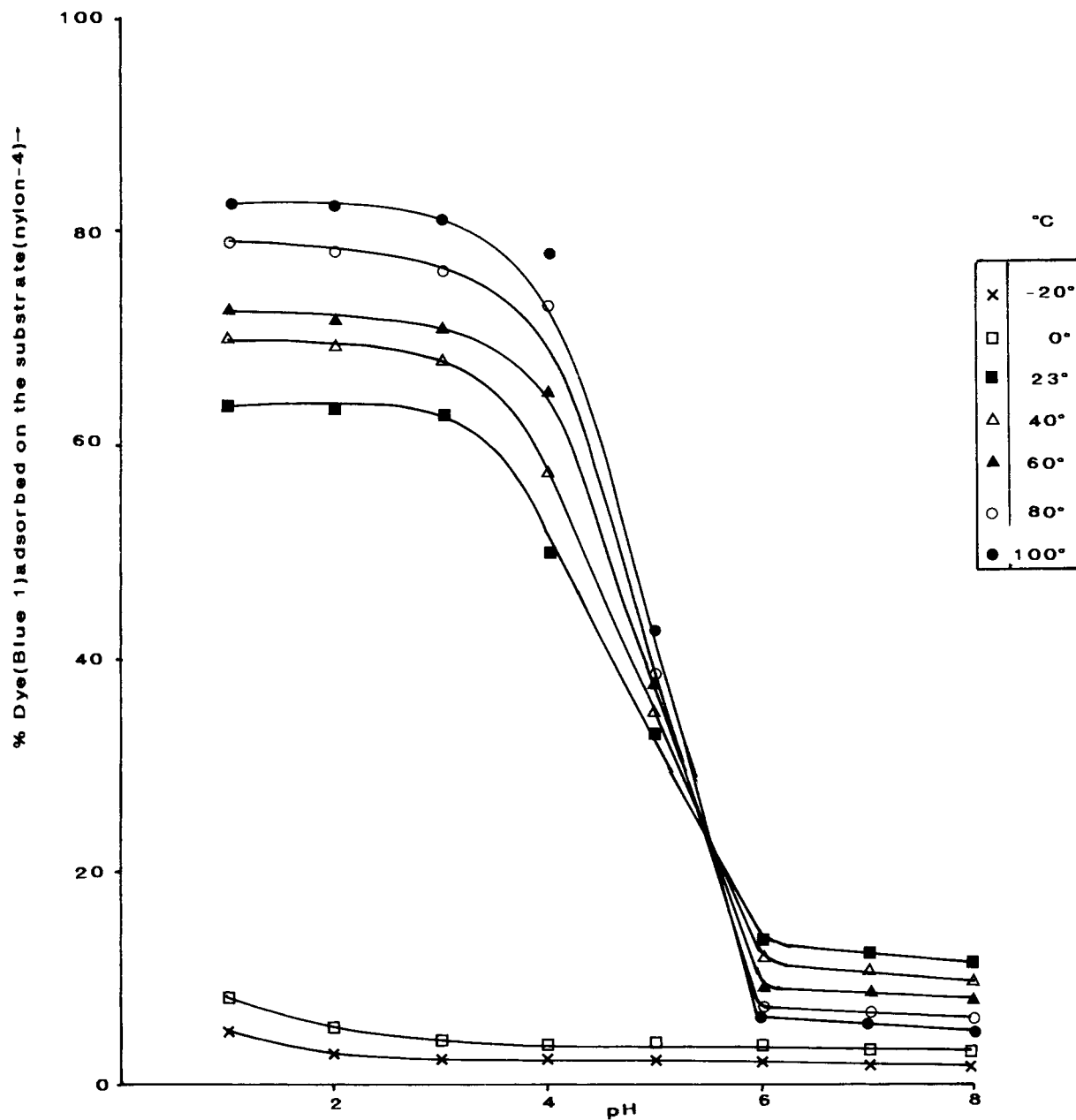


Figure 3 Effect of temperature on the adsorption of Blue 1 on nylon 4 after 2 h (exposure time) within a pH range 1-8.

2.4. Temperature Effect

The same procedure was followed for the preparation of the dye solutions as in the case of the pH variation experiments. Exposure temperatures of the substrates were -20 , 0 , 23 , 40 , 60 , 80 , and 100°C for 2 h.

2.5. Determination of Dye Migration Rate

Solutions of dye (Brilliant Blue, No. 1) of 20 ppm concentration were adjusted to pH 3.0 using a 1.0M

citric acid solution. Substrates of nylons 6 and 7 were exposed to the solutions at 0 , 25 , 50 , and 100°C for a time range of 20, 40, 60, 80, and 100 and 120 min. The action of the adsorption was stopped by immersing the substrates into liquid nitrogen recipients.

2.6. Determination of Migration Mechanism

Seven solutions of 20 ppm Blue No. 1 were prepared from the stock solution. The pH of each solution was adjusted to 3.0 with one of the following acids²⁴:

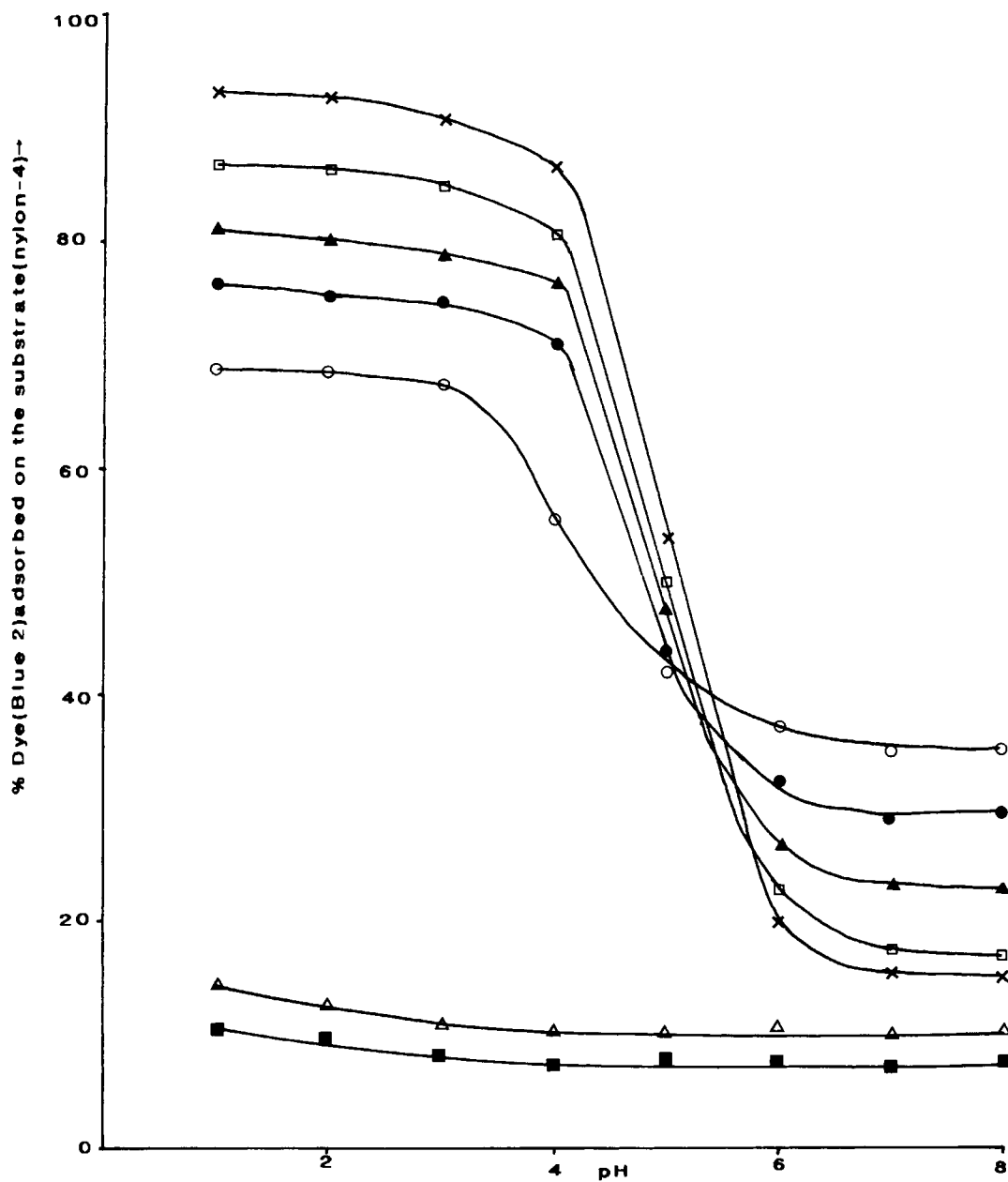
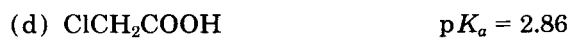
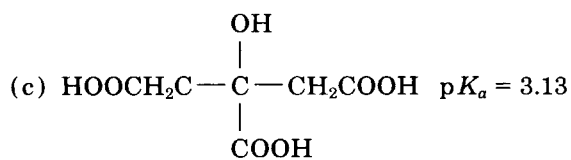


Figure 4 Effect of temperature on the adsorption of Blue 2 on nylon 4 after 2 h (exposure time) within a pH range 1–8. For symbols, see Figure 3.



Exposure time and temperature of the polyamides (nylons) substrates were 2 h and 23°C, respectively.

2.7. Additive Effect

Solutions of 20 ppm dye were prepared from stock solutions and the pH of each solution was adjusted to pH 3.0 with 1.0M citric acid.

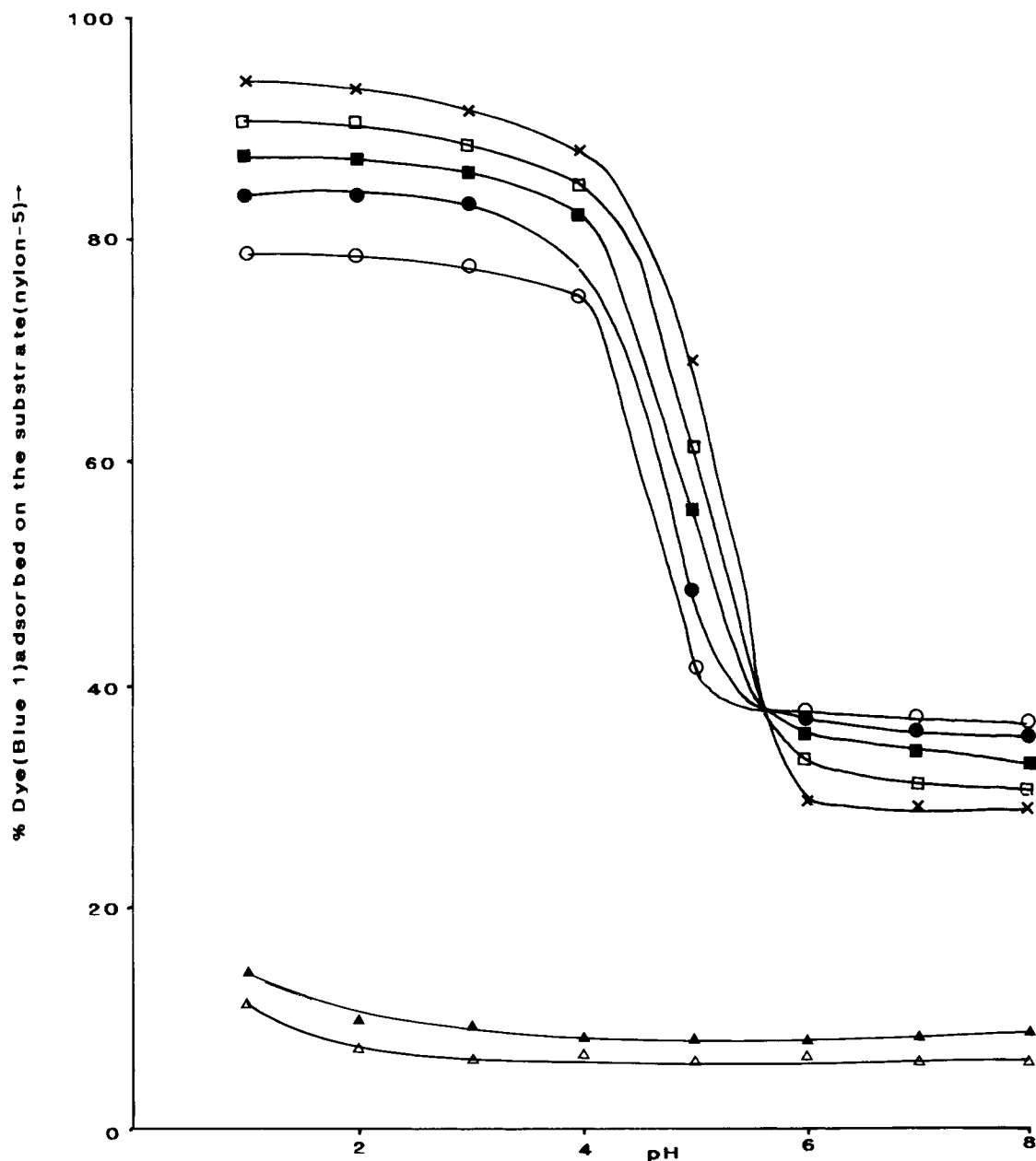


Figure 5 Effect of temperature on the adsorption of Blue 1 on nylon 5 after 2 h (exposure time) within a pH range 1-8. For symbols, see Figure 3.

Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), potassium chloride (KCl), and potassium sulfate (K_2SO_4) powder were added to produce a series of solutions of a range 0.1-10M salt. A series of sugars such as glucose, fructose, xylose, and sorbitol were added to produce solutions within the concentration range 0.1-1.0M.

2.8. Apparatus

An Orion pH meter was used for the pH measurements. An Ahiba WBRG 60 Texomat (Ahiba,

Charlotte, NC) was used for dyeing purposes. The dye uptake by the substrates was indirectly measured by estimating the remaining amounts of the dye in the solutions using a Pye-Unicam SP 1700 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. pH Effect

The pH of the dye (I) and (II) solutions was varied within a relatively wide range (2-8). The pH was

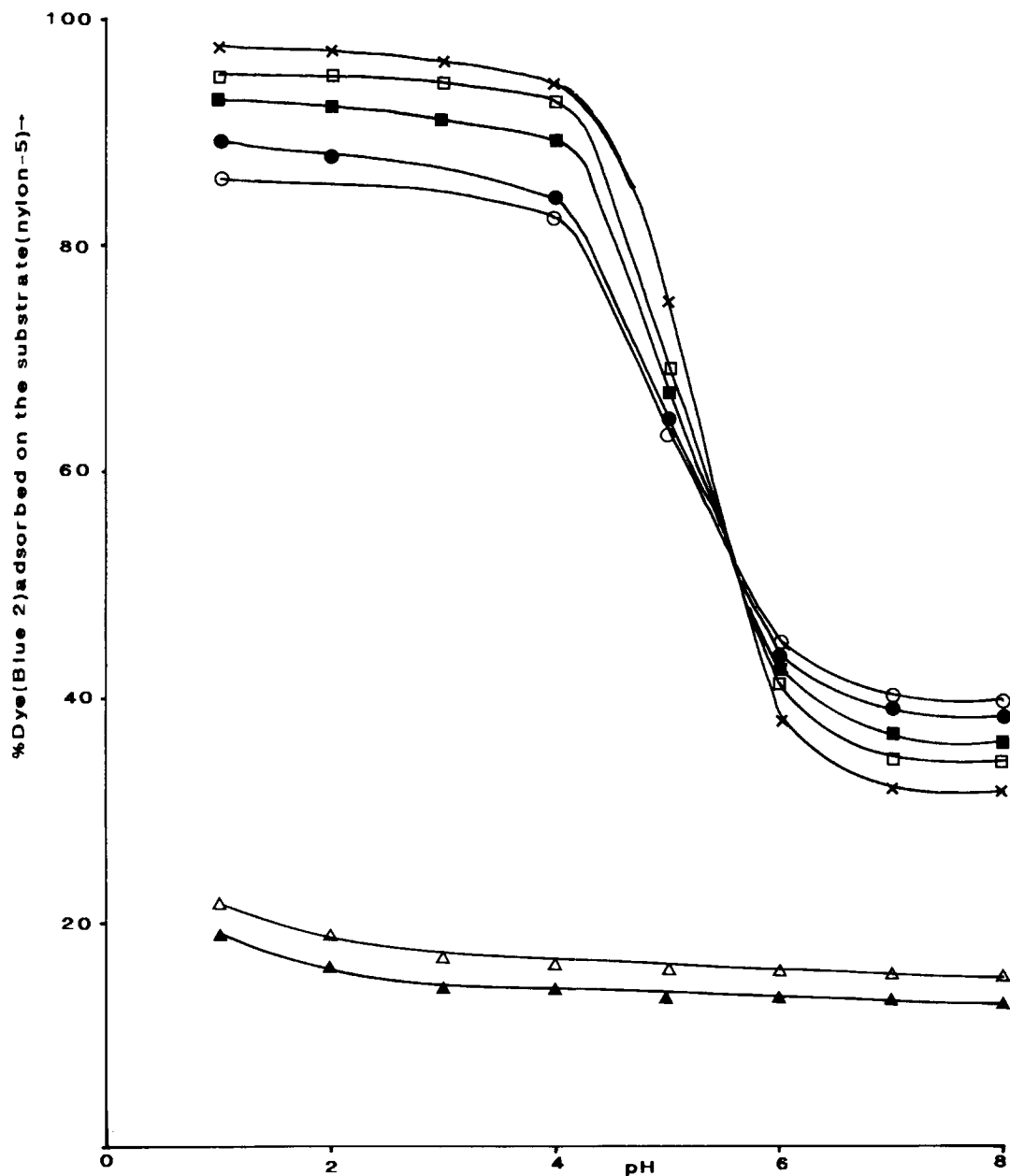


Figure 6 Effect of temperature on the adsorption of Blue 2 on nylon 5 after 2 h (exposure time) within a pH range 1-8. For symbols, see Figure 3.

found to have a substantial effect on the migration of the dye to packaging polyamides. The results are illustrated in Figures 1 and 2. The following order was observed for both dyes' uptake (at pH from 2 to 8) by different substrates polyamides within 2 h exposure time:

- (a) even number: nylon 4 > nylon 6 > nylon 10 > nylon 12
- (b) odd number: nylon 5 > nylon 7 > nylon 9 > nylon 11

The higher number of —NH_2 end groups was considered responsible for the electrostatic interaction promoting the (a) and (b) sequences.

Table I shows the average amine end groups of the eight polyamides used as substrates in this study. The results in conjunction with the dye uptake values illustrated in Figures 1 and 2 are in good agreement with similar data in the literature.¹ The influence of pH on the dye adsorption was also studied at different temperatures (Figs. 3-6) and the results showed a dominating effect of temperature on the

Table II Acids Used for the pH Adjustment and Their pK_a

Acid	CH_3COOH	$CH_3CH_2CHClCOOH$	$ \begin{array}{c} OH \\ \\ HOOC - H_2C - C - CH_2COOH \\ \\ COOH \end{array} $	$ClCH_2COOH$	$Cl_2CHCOOH$	Cl_3CCOOH	H_2SO_4
pK_a	4.74	3.8	3.13	2.86	1.26	0.64	-5.2

pH. Very low temperatures (-20 and $0^\circ C$) can minimize the extent of dye adsorption on the substrate at all the pHs.

Anionic dyes are applied to polyamides within the pH range 3–8. Previous publications^{24–26} showed that protons diffusing from dilute aqueous solutions

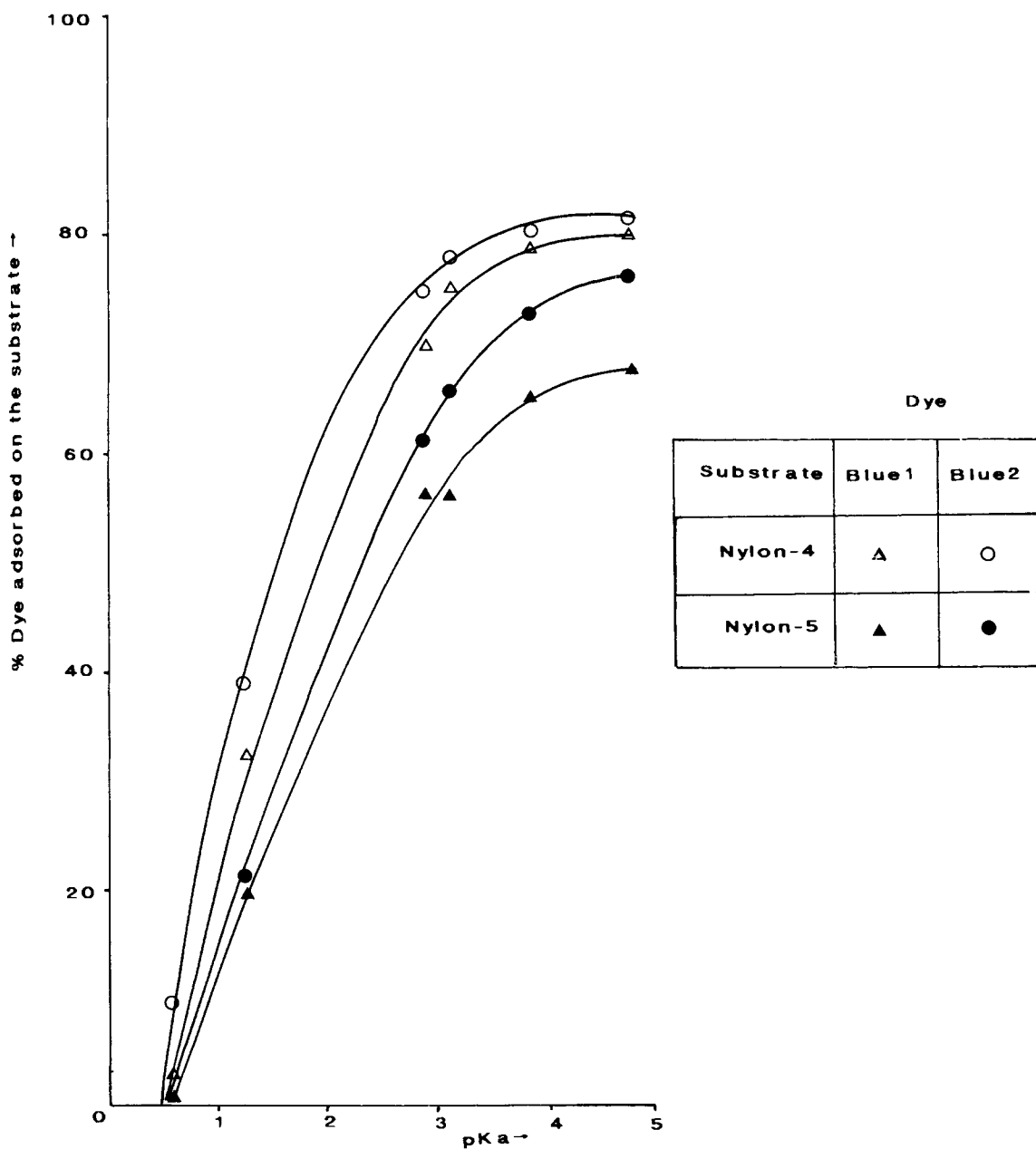


Figure 7 Effect of pK_a (weak/strong acids) on the adsorption of dyes (Blue 1 and Blue 2) on nylons 4 and 5 at pH 4 after 2 h (exposure time).

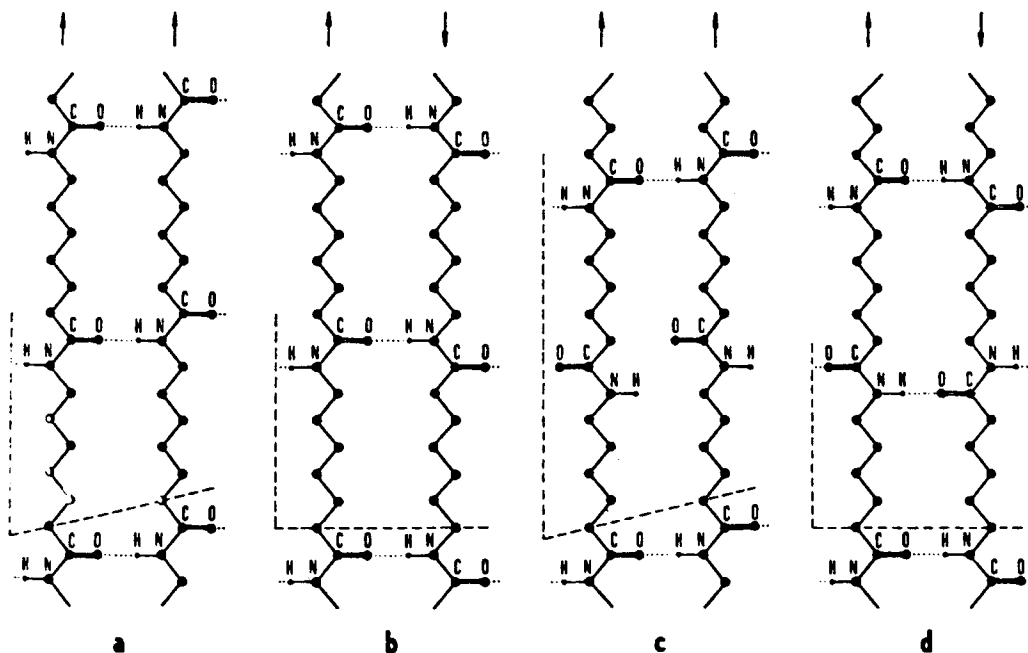


Figure 8 Models of hydrogen bonding in nylons with even (a, b) and odd (c, d) numbers of CH_2 groups.

of an acidic medium protonate the basic groups of polyamides. At its isoelectric point, nylon contains an equal number of negatively charged carboxylic acid and positively charged amine end groups. When the nylon is placed in an acid solution, ionization of the carboxylic groups is depressed, leaving the polyamide with a net positive charge. The positive charges are initially neutralized by the rapidly moving acid anions and these are then slowly displaced by the relatively slowly moving high-affinity dye anions.

Investigations in this field have demonstrated that above pH 3 the adsorption probably occurs by two mechanisms that proceed simultaneously:

- (i) adsorption on amine end groups (primary reaction); and
- (ii) adsorption by hydrogen bonding to amide groups.

Below pH 3, the amide groups in the polyamide chain can be also protonated and provide additional ionic dye sites.^{27,28} To provide further evidence for the adsorption mechanism, the relationship between the $\text{p}K_a$ of the acids used for the pH adjustment to the dye uptake was also studied. The acids used in the study and their $\text{p}K_a$ are given in Table II. The results are illustrated in Figure 7. Figure 7 shows that weak acids (i.e., acetic or citric acid) are fa-

voraging the sorption of the dye. This can be attributed to the fact that weak acids are adsorbed (connected) by nylon to a greater extent than are strong ones at the same pH, even in an undissociated form by hydrogen bonding to the amide groups.²⁵ Thus, sites other than end amine groups would be enabled to bind with dye molecules.

3.2. Correlation between Dye Uptake and the Polyamide Structure

The differences observed at the level of the dye uptake between the odd- and the even-numbered polyamides should be interpreted mainly in terms of their structure. The odd-numbered polyamides crystallize in the α and β forms. The difference between the two forms lies in the side-by-side packaging of the sheets. Molecular sheets are placed one upon the other in the α -form, whereas the β -form is of minor importance because it is metastable. In both the α - and β -forms, the triclinic structure prevails with the formation of parallel and antiparallel chains.

The formation of hydrogen bonding between $\text{C}=\text{O}$ and $\text{N}-\text{H}$ (i.e., $\text{C}=\text{O} \cdots \text{H}-\text{N}$) is by far more difficult and more easily disrupted in the case of odd- than of even-numbered polyamides where the order of crystal planes prevails, as can be seen from Figures 8 and 9. This reasoning is also corroborated by the lack of order in the crystalline

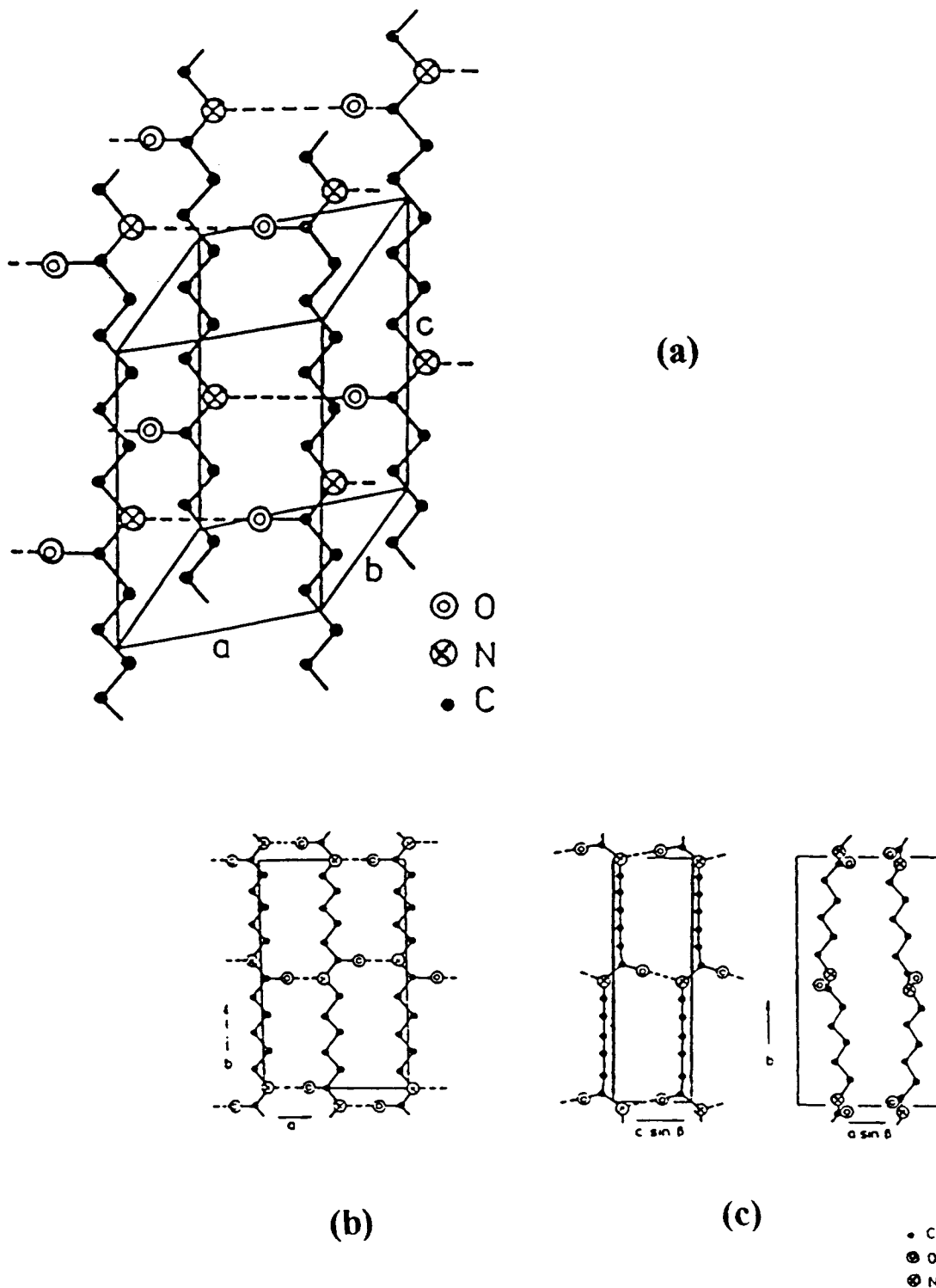


Figure 9 (a) The structure of nylon 7 and (b and c, respectively) structures of alpha and gamma (α , γ) polymorphs of nylon 6.

phase of polyamides 7 and 11 caused by interposition of irregular sheets (consisting of both parallel and antiparallel chains.²⁹⁻³⁵ Therefore, the odd-num-

bered polyamides were expected to exhibit a more pronounced dye uptake than were the even ones, as was actually the case (Figs. 1 and 2).

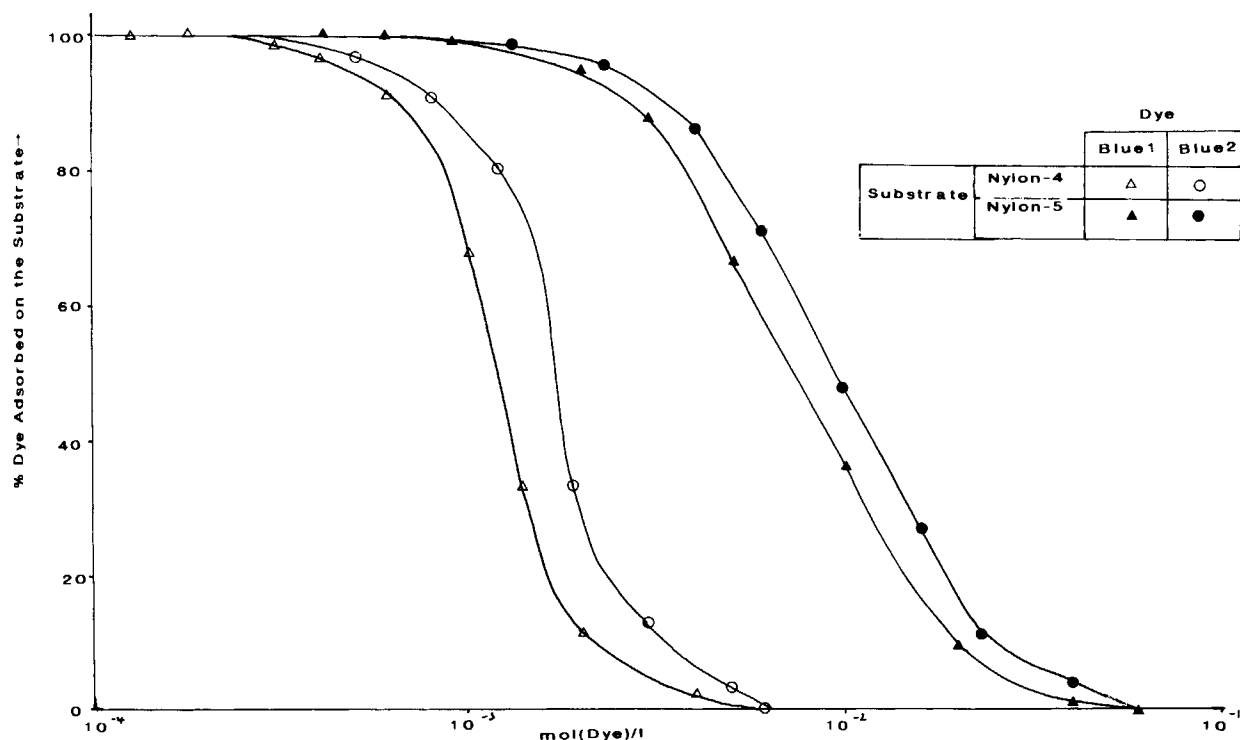
Table III Adsorption of Dye (Blue 1) on (a) Nylon 4 and (b) Nylon 5 at Different Temperatures after 2 h and at pH 1, 3, 5, and 7

Temperature (°C)	Dye Uptake (%) on Substrates (a) and (b)							
	(a) Nylon 4				(b) Nylon 5			
	pH 1	pH 3	pH 5	pH 8	pH 1	pH 3	pH 5	pH 8
-20	5.0	2.5	2.5	1.1	11.2	6.0	5.8	5.6
0	8.0	4.0	4.1	2.5	13.9	8.1	7.2	7.4
23	63.5	62.5	32.8	4.9	78.5	77.6	41.3	28.6
40	70.0	68.0	35.0	6.0	84.0	83.5	47.9	30.3
60	72.5	71.0	37.4	7.6	87.4	86.2	55.6	32.7
80	79.0	76.5	38.7	9.5	90.5	87.9	61.1	35.1
100	82.5	81.0	42.5	11.5	94.5	92.1	68.9	35.9

A similar sequence for the dye-uptake values was observed for nylons 4 and 5 at various temperatures and pHs (Table III). The differences between the members of the same series (odd- or even-numbered polyamides) could be attributed to both a higher number of available amide groups and amine end groups^{36,37} (Table I).

The percentage crystallinity of the substrate was also investigated because it is known that the dif-

fusion of the dye is by far easier in the amorphous regions than in the crystalline ones.^{25,38} However, in the polyamides under study, the percentage crystallinity was found to lie within the same range of 30–40% (Table I, average from X-ray diffraction patterns³⁹ and differential scanning³⁹ calorimeter measurements), which does not allow us any further speculation in this direction for interpreting the results.

**Figure 10** Effect of dye concentration (mol/L) on the adsorption of dyes (Blue 1 and Blue 2) on nylons 4 and 5 at pH 4, at 23°C and after 2 h (exposure time).

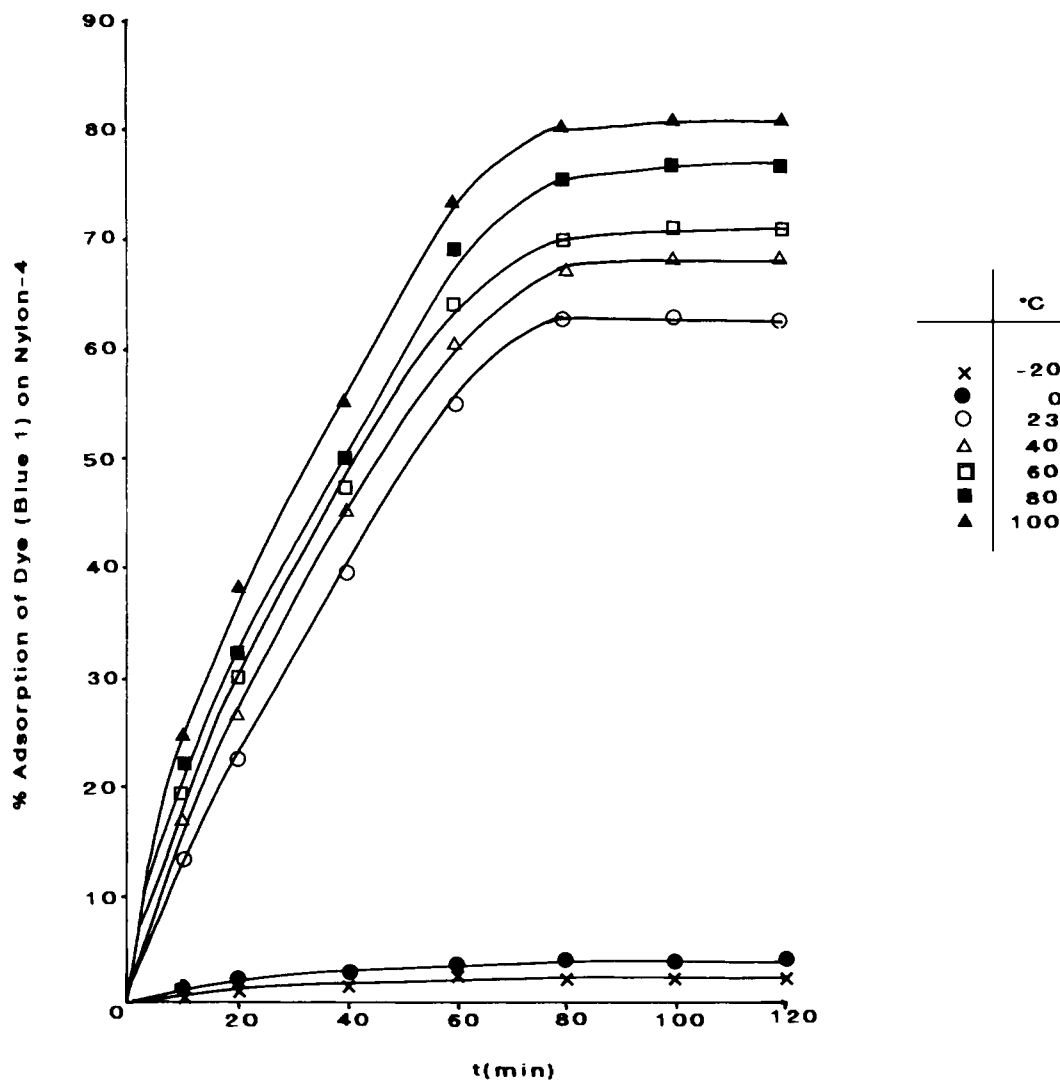


Figure 11 Isothermal adsorption of Blue 1 on nylon 4 vs. time at pH 3.

3.3. Dye Concentration Effect

The influence of the concentration of the dye solutions (Blue 1 and Blue 2) on the adsorption of the dye on the substrate (nylons 4 and 5) was studied and the results are illustrated in Figure 10.

Figures 11 and 12 illustrate the dye uptake dependence upon the number of amine end groups and carbonyl groups when the concentration of the dye solution varied. An increase in amine and carbonyl end groups caused the removal of the dye from the solutions, as has already been mentioned. The number of sulfonic groups of the dyes was also shown to favor the exhaustion of the dyes (Table IV) since the sulfonic groups are the anionic groups, mainly responsible for the dye sorption on the substrate. Therefore, an increase in dye concentration pro-

moted an increase in the number of sulfonic groups available for ionic bond formation between the dye and the polyamide.⁴⁰

3.4. Temperature Effect

The influence of temperature on the dye adsorption on the polyamides was studied for Blue 1 and nylons 4 and 5 at pH 7. The results are given in Table III. Table III shows that a temperature increase results in an increase in the dye adsorption, as was expected from similar data in the literature.^{1,38}

The effect of temperature upon the dye removal from the solution was critical. However, no temperature range was detected within which no dye depletion occurred. From Table III it is also concluded

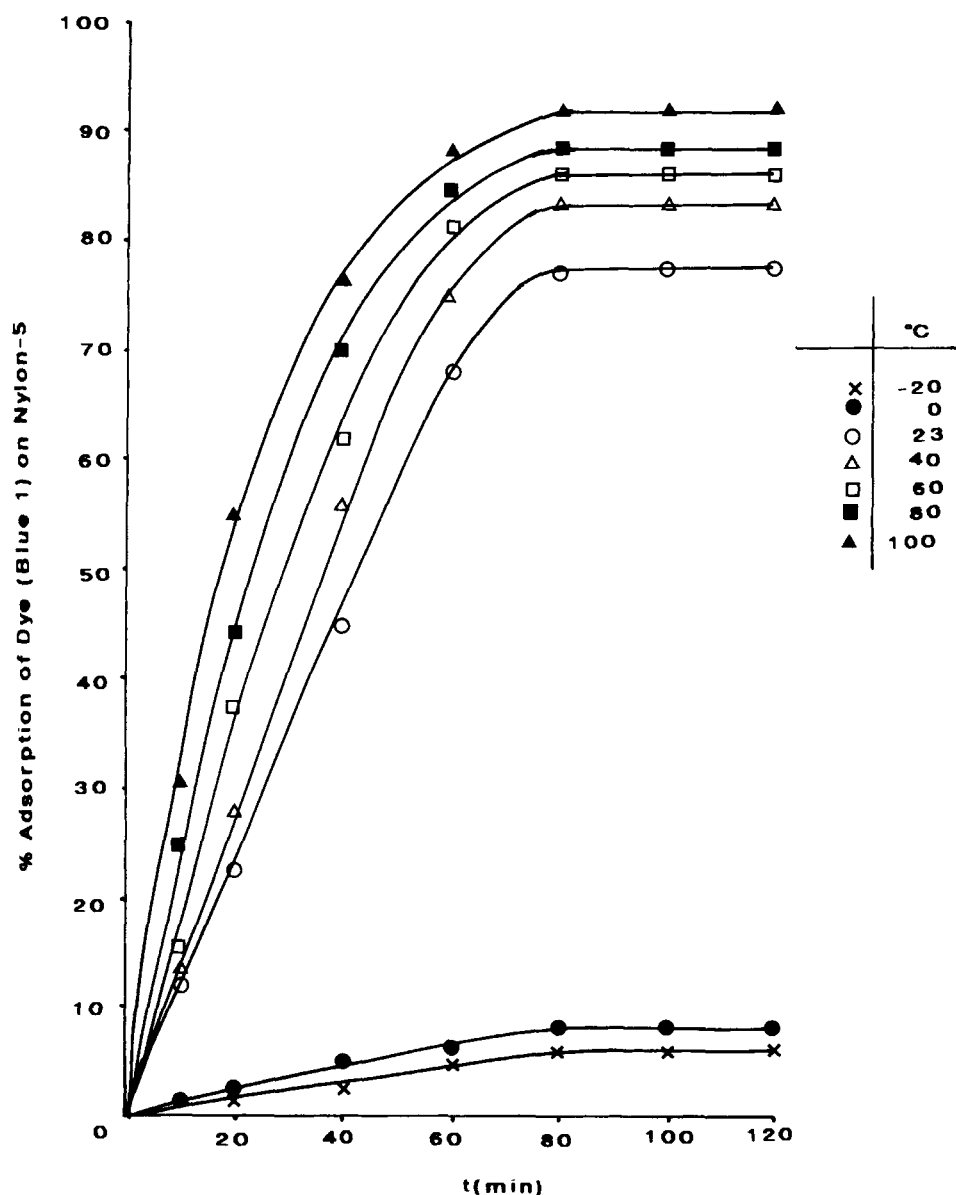


Figure 12 Isothermal adsorption of Blue 1 on nylon 5 vs. time at pH 3.

that the dye uptake for the odd-numbered polyamide nylon 5 is higher than that for the even-numbered nylon 4 at all the temperatures and the pHs studied.

The effect of the temperature on the dye uptake was also studied at different pHs for the above polyamides (Figs. 3-6). This study has shown that at pHs > 6 the dye adsorption generally decreases in all the temperatures, but even at pH 8 and temperature of -20°C , there is a minimum percentage of dye absorbed by both the odd- and even-numbered polyamides.

3.5. Determination of Dye Adsorption Rate

There are mainly two methods describing the determination of the dyeing rate, which have been de-

scribed in detail by other workers.^{38,42-44} According to the first method,³⁸ the rate of the process is described by a velocity constant. Among the several empirical equations that have been suggested as giving a fairly good fit to the rate of dyeing curves are the hyperbolic eq. (1):

$$Kt = \frac{1}{A^{\infty} - A} - \frac{1}{A^{\infty}} \quad (1)$$

where A is the percentage of dye adsorbed on the fiber at a time t ; A^{∞} , the equilibrium exhaustion; and k , the arbitrary velocity constant, and the exponential eq. (2):

$$A = A^{\infty} (1 - e^{-k \cdot t}) \quad (2)$$

	Nylon-4+Glucose/NaCl	Nylon-5+Glucose/NaCl
Blue 1	Δ	○
Blue 2	▲	●

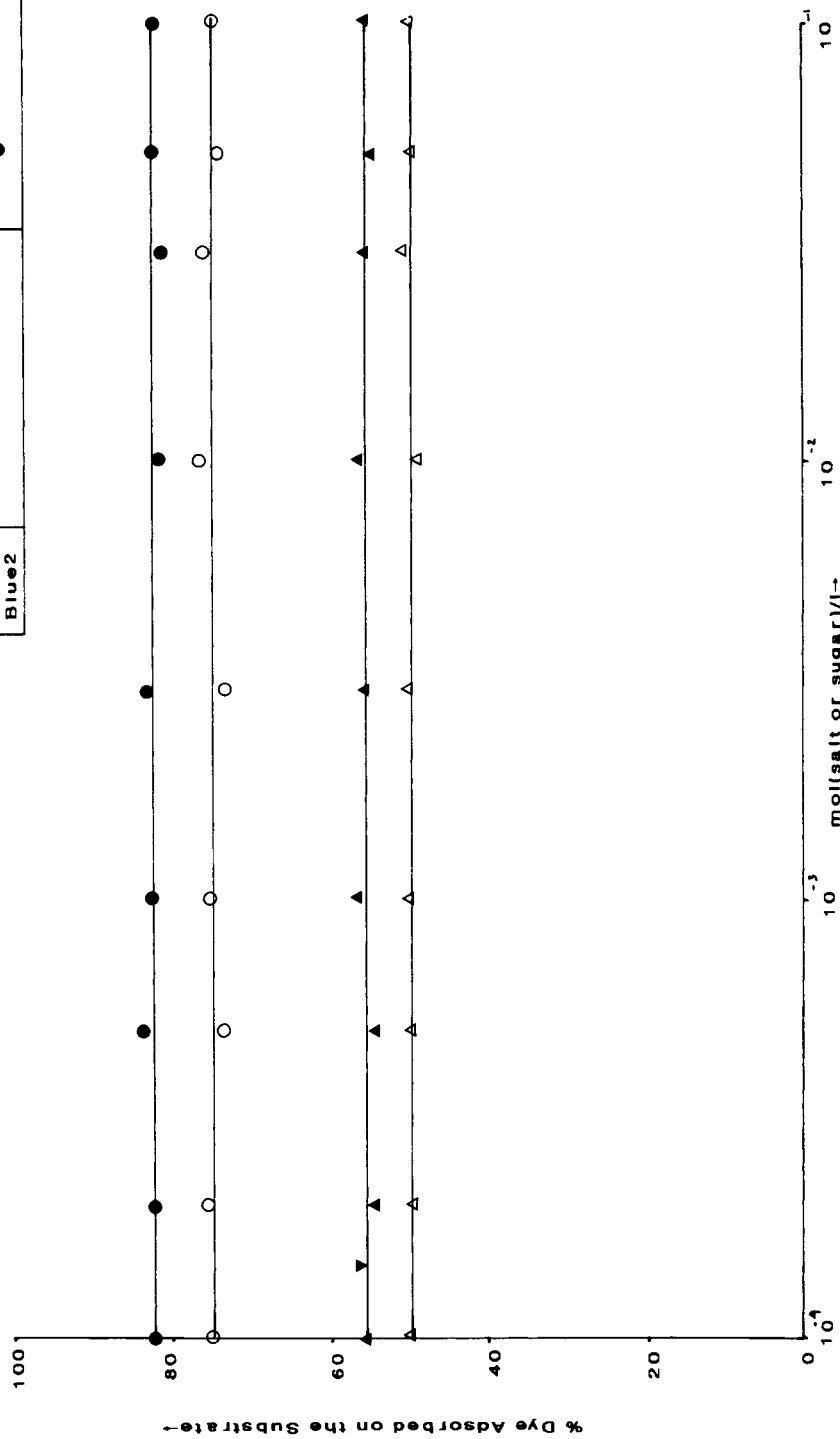


Figure 13 Effect of additives (glucose, sodium chloride) on the adsorption of dyes (Blue 1 and Blue 2) on nylons 4 and 5 at pH 4 and T 23°C.

Table IV Dye Uptake (ppm) by Substrate (Nylons 4 and 5) at 23°C for a pH Range 1–8

Dye	No. of Sulfonic Groups	pH 1		pH 3		pH 4		pH 5		pH 8	
		Nylon 4	Nylon 5	Nylon 4	Nylon 5	Nylon 4	Nylon 5	Nylon 4	Nylon 5	Nylon 4	Nylon 5
Blue 1	2	38.7	56.7	37.2	54.6	30.0	45.0	18.6	30.9	6.6	15.6
Blue 2	3	47.4	58.5	43.2	57.0	33.6	49.5	22.5	35.7	13.5	19.8

Once the velocity constant (K) has been determined, the activation energies of dyeing were calculated from eq. (3):

$$K = K_0 \cdot e^{-\Delta H/RT} \quad (3)$$

where K is the velocity constant at a time t ; K_0 , the velocity constant at time t_0 ; ΔH , the activation energy of dyeing at temperature T ; and R , the universal gas constant ($8.314 \cdot 10^{-3} \text{ kJ mol}^{-1} \text{ deg}^{-1}$).

The logarithmic form of eq. (3) is

$$\ln K = \ln K_0 - \Delta H/RT \quad (4)$$

Hence, the logarithm of the observed velocity constant at different temperatures was plotted against the reciprocal of the absolute temperature; a straight line was derived, the slope of which is equal to $\Delta H/R$, from which the activation energy of dyeing was determined. The activation energies of dyeing nylons 4 and 5 with Blue 1 at pH 3 were found to lie within the range $0.2\text{--}2 \text{ kJ mol}^{-1}$, which are significantly lower compared to previous values for acid dyes on wool ($19.76\text{--}46.60 \text{ kJ mol}^{-1}$)⁴² and for dispersed dyes on nylon fiber ($83.68\text{--}98.97 \text{ kJ mol}^{-1}$).³⁸ Therefore, the applicability of eqs. (1) and (2) in the case of our experiments should, rather, be ruled out and the

Table V Half-Dyeing Times ($t_{1/2}$) for Nylons 4 and 5 by Blue 1 at Different Temperatures

Temperature (°C)	$t_{1/2}$ (min)	
	Nylon 4	Nylon 5
−20	19.0	40.0
0	18.0	26.2
23	27.0	32.5
40	28.0	31.0
60	26.0	25.5
80	26.5	26.0
100	24.0	17.5

second method of describing the dyeing rate should be adopted. This method consists of giving the time/adsorption isotherms of the sigmoid type (Figs. 11 and 12). To give numerical values to this rate, a convenient method involving no assumption as to mechanism is to determine the time of half-dyeing ($t_{1/2}$). This is the time required for the fiber to absorb half as much dye as it will absorb in the equilibrium state.³⁸ The method of determining $t_{1/2}$ and A was to measure first the equilibrium exhaustion by inspection of the rate of the dyeing curve (Figs. 11 and 12) and then to determine from the curve the time at which the adsorption $A/2$ occurred. Table V gives the half-dyeing times ($t_{1/2}$) for nylons 4 and 5 (range 17.5–40 min), whereas the A^∞ (exhaustion/equilibrium percentage of dye upon the fiber) was given previously in Table III.

3.6. Effect of Additives

The influence of the addition of a sugar solution (glucose) at different concentrations on the adsorption of Blue 1 and Blue 2 on nylons 4 and 5 is illustrated in Figure 13. Figure 13 shows that the addition of the salt (NaCl)/sugar (glucose) solution, as well as its concentration variation, does not alter the amount of dye adsorption on the polyamide in the absence of the additive. This observation is in agreement with the conclusions of a previous study carried out with the same dyes and using polycaprolactam (nylon 6) as substrate.¹

4. CONCLUSION

The utilization of polyamides as food-packaging materials might present some staining problems in case they are used in contact with foods containing acid dye solutions. Low storage temperature of packaged foodstuffs, low number of amine end groups (available for protonation), and absence of acid medium are the main requirements, established

from this study, for avoiding undesirable staining upon the polyamide packaging.

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