Effect of Additional Hydroxyl Groups on Dissolution of Azo Dyes Derived from N-Carboxylic Acid-1,8-Naphthalimide in Aqueous Solutions Containing Various Surface Active Agents

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ABSTRACT

Dissolution of azo dyes derived from N-carboxylic acid-1,8-naphthalimide was studied in aqueous solutions containing formaldehyde condensation of naphthalenesulphonic acid and fatty alcohol ethylene oxide compound surfactants. The effect of additional hydroxyl group on chemical structure of dye on dissolution was also investigated. In addition, the effect of important factors on dissolution of used dyes in surfactant solutions such as the concentration of surfactants, temperature and time were considered. The results revealed that the dissolution rate of both dyes in formaldehyde condensation of naphthalenesulphonic acid was greater than the fatty alcohol ethylene oxide compound. In the same circumstance, the dissolution values of dyes indicated that dye 2 containing N-ethyl-n-(2-hydroxyethyl) aniline had more solubility than dye 1 containing N,N-diethylaniline. It may be attributed to the greater hydrophilicity of the dye 2 compared to dye 1. The results suggested that the dissolution of dyes in water containing surfactants was dependent on the chemical structure of dyes and the type of used surfactants. Prog. Color Colorants Coat. 6(2013), 67-79. © Institute for Color Science and Technology.

1. Introduction

Disperse dyes were introduced for the dyeing of cellulose secondary acetate and subsequently were found to be useful for the dyeing of other synthetic fibers as well [1, 2]. The disperse dyes are almost the main class of dyes for coloration of polyester, the number one synthetic fiber regarding the production volume and usage. Disperse dyes have very slightly solubility in water at room temperature and therefore require the presence of a dispersing agent for enhancing their solubility [3]. The dispersing agents decrease the dye particle size and facilitate the change of dye powder to fine dispersion during dyeing process. This prevents the coalescence of dispersed particles and agglomeration. The disperse dyes are considered to dye fibers via a solid solution mechanism. Every disperse dye dissolves in the fiber independent from other disperse dyes [4]. There is still

some doubts about the mechanism of the dye releasing from the disperse media on the fiber, i.e., via direct contact between micelles and fiber surface or adsorption of single molecules from the continuous aqueous phase.

In the field of textiles, however, various types of surfactants are utilized in dyeing or finishing processes; the way of utilizing them depends usually upon previous experience. In dyeing processes, the role of surfactant is especially very significant [6, 7]. The main interest is the characteristic behaviors of surfactants which give a good level of dyeing and increase fastness of dye on fiber [7]. Main functions of the surfactant used in dyeing as an auxiliary product can be divided to four types of actions: (1) as a surface active compound, namely dissolution, dispersing and wetting; (2) as a fiber affinity compound, similar to colorless dye; (3) as a dye affinity compound; and (4) as both fiber and dye affinity compound [1, 7]. In order to reorganize the roles of surfactants in dyeing, it is essential to investigate the effect of important factors in dissolution of dyes, especially in disperse dyes such as temperature of the aqueous media, process time and surfactants concentration.

The dissolution value of pure disperse dye is generally very low if the dye is present as large particles or crystallites in the solution. For acceptable rate of dyeing, the size of the dye particles should be in sub-microns range and kept in a stable state by addition of appropriate dispersing agent. For this purpose, anionic and nonionic dispersing agents are two major classes of surfactants to dyeing of textile fibers [8]. From a practical standpoint, the rate-determining step of dyeing process may be either the rate of dissolution of the dye, or alternatively the rate of diffusion of the dye into the fiber. The role of dispersing agents is very important in both rate-influential steps of hydrophilic and hydrophobic dyeing process of the fibers [1].

Several studies are available on properties and applications of dispersing agents in the dyeing of hydrophobic fibers with disperse dyes [9-11]. The dissolution of disperse dyes in the presence of surfactants and interactions between the dye and the surfactant via spectrophotometry method have been researched previously [12-14]. Different types of anionic and nonionic surfactants have been utilized in this regard [15-17]. The solubilization data and concentration effectiveness of surfactants provide useful information in preparing dispersions of dyes in aqueous solution and in the dyeing of hydrophobic fibers. Suitable dispersions and dye solubility in solution are necessary factors for uniform adsorption of disperse dyes onto the substrates [8].

Recently, the disperse dyes based on the azonaphthalimide chemical structure have been introduced as the good candidates for dyeing polyester fabrics. The presence of the naphthalimide system leads to production of a deep and intense color and bathochromic effect rather than azo dyes containing benzene rings [18, 19]. In order to increment the hydrophilicity of disperse dyes, some groups such as hydroxyl and carboxylic acids were added to their chemical structures. The dyes with weak carboxylic groups and molecular weights of 300-500 (g/mol) can be applied for dyeing both wool and polyester fibers with excellent leveling and very good wet-fastness properties [20, 21]. However, the presence of carboxylic acid groups in the chemical structure does not guarantee the usage of dye for wool/polyester dyeing as they have low solubility in water [22,23]. Hence, the presence of the appropriate dispersing agents for employing these dyes is necessary.

In previous works, we reported results of dissolution of some monoazo naphthalimide disperse dye containing N-carboxylic acid and N-alkyl groups in the presence of anionic and nonionic dispersing agents [24, 25]. However, we didn't study, the effect of hydroxyl groups in coupling component on dissolution of monoazo naphthalimide dyes. Therefore, in this study we report dissolution kinetic of two monoazo N-carboxylic acid naphthalimide dyes in aqueous naphthalene sulfonate and polyether surfactants, and also investigate the effect of additional hydroxyl group in coupler on dissolution of dyes in water containing various surfactants.

2. Experimental

2.1. Materials and apparatus

In this paper, the chemicals were of analytical grade and purchased from Merck and Aldrich Companies. The commercial formaldehyde condensation of naphthalenesulphonic acid (surfactant 1) and fatty alcohol ethylene oxide compound (surfactant 2) as the surfactants were provided from Ciba Co without further purification.

2.1.1. Synthesis of dyes

In this study, the dyes were prepared from acenaphthene according to our previous work [26]. The synthesis method and the characterization data of these dyes can

also be found in detail elsewhere [26]. The chemical structure of the dyes is depicted in Figure 1.

2.2. Measurement method

Different concentrations of surfactants (0.1%, 0.5% and 1%) were prepared using distilled water. 0.01 g of the finely powdered dye and 50 ml of surfactant solutions were mixed together in an Erlenmeyer at different temperatures (25, 40, 60 and 80 $^\circ$C) using a shaker. The samples were withdrawn from the solution at certain time intervals, filtered off using a glass fiber (Advantec GA55, pore size of 0.6 μm). The filtrate was diluted with acetone (1:1) and analyzed at the wavelength of maximum absorbance of dyes by UV-Vis spectrophotometer.

For solubility studies, an excess amount of pure naphthalimid dye (0.01 g) was added to an aqueous solution of surfactant (50 mL) at different concentrations (i.e. 0.1%, 0.5% and 1%) and was shook in a water bath incubator (IKA) at different temperatures (25, 40, 60 and 80 $^\circ$C). The samples were withdrawn from the solution at certain time intervals and filtered off using a glass fiber (Advantec GA55, pore size of 0.6 μm). The filtrate (1 mL) was mixed with 4 mL of acetone and then absorbance measurements were carried out on Cecil 9200 double beam UV-VIS spectrophotometer.

Absorption data readings were taken at the wavelengths of maximum absorbance for each of the solutions (i.e., for Dye 1, 536 nm and for Dye 2, 523 nm). Separate calibration curves were prepared for each

of the two dyes in water and acetone (1:4) mixture. The amount of dye dissolved in surfactant solutions was calculated using the calibration curves.

3. Results and discussion

The effect of three important factors such as time, concentration of surfactants and temperature on dissolution of used dyes was examined. Figure 2 shows that the amount of dissolved dye in both surfactants increases by time at 80 $^\circ$C. Dyes represents better solubility in water containing surfactants relative to N-alkyl-1,8-azonaphthalimide disperse dyes [25]. The presence of carboxylic acid group in dye molecules causes the hydrophilicity of these dyes to increase. The carboxylic acid moiety is debated to be a highly polar organic functional group. This polarity results from the presence of a strongly polarized carbonyl (C=O) and hydroxyl (O-H) groups. It is clear that oxygen is a relatively electronegative atom and when covalently bound to carbon and particularly to hydrogen, a strong permanent dipole is created. In the case of carboxylic acids, the polarization of the O-H group is even stronger than the O-H group of alcohols due to the presence of the adjacent carbonyl moiety. The dipoles present in carboxylic acids allow these compounds to participate in energetically favorable hydrogen bonding interactions with water molecules. It is clear that the carboxylic acid group presents on dye molecule is able to form hydrogen bonding with water molecules. Therefore, dissolution of dye molecule in water will increase.

Dye	Y
1	$N(CH_2CH_3)_2$
2	$N(CH_2CH_3)(CH_2CH_2OH)$
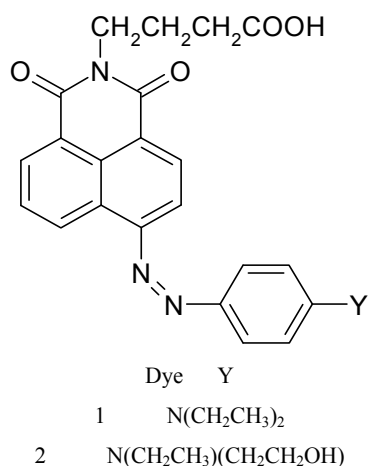
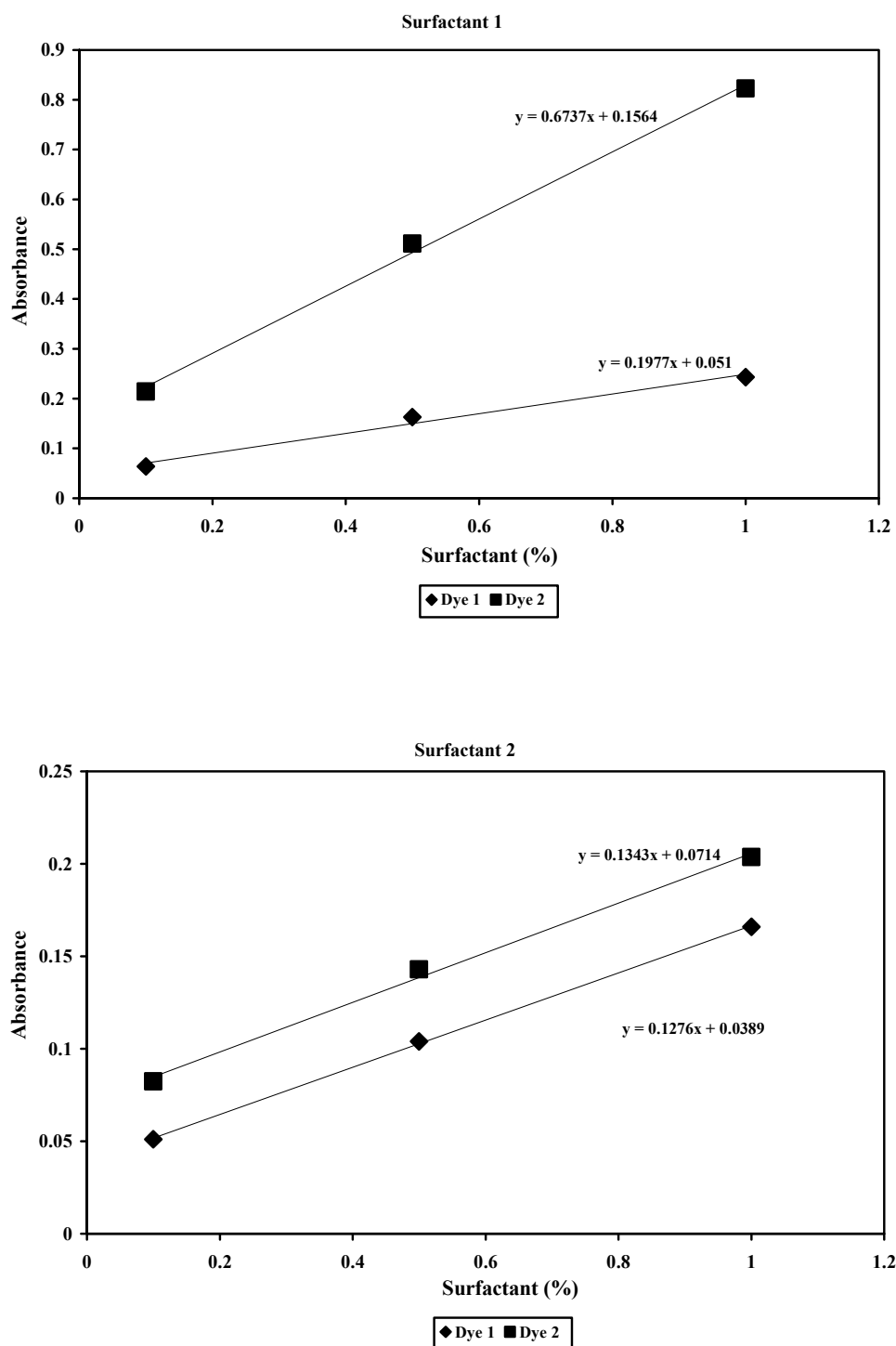**Figure1:** The chemical structure of dyes.
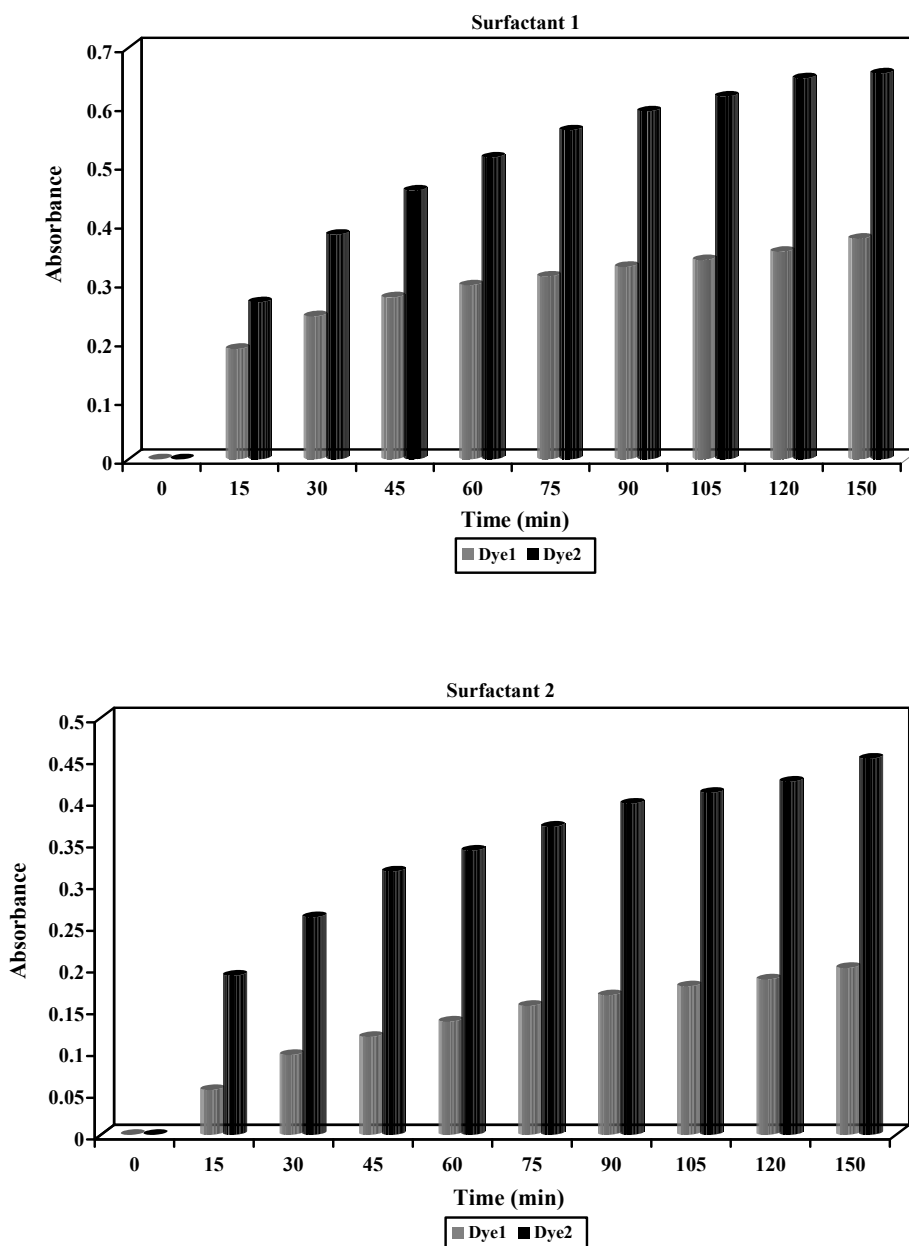
Figure 2: Dissolution of dyes in surfactant solutions (1%) at 80°C (dye initial concentration=0.2 g/L).

The amount of dissolved dye 2 in both of surfactant solutions was greater than dye 1. This can be attributed to the chemical structure of dye 2 which has an additional hydroxyl group in comparison with dye 1. This group can form hydrogen bonding with H_2O molecules. However, the solubility of dyes in water containing formaldehyde condensation of naphthalenesulphonic acid surfactant was greater than that of fatty alcohol ethylene oxide. On the other hand, the dissolving power of

formaldehyde condensation of naphthalenesulphonic acid surfactant was higher than fatty alcohol ethylene oxide.

The effect of surfactant concentration and temperature on dissolution of dyes is illustrated in Figures 3 and 4, respectively. The results clearly represent that the solubility of dyes in the presence of formaldehyde condensation of naphthalenesulphonic acid and fatty alcohol ethylene oxide is highly related to concentration of surfactants and temperature.

Surfactant 1

$y = 0.6737x + 0.1564$

$y = 0.1977x + 0.051$

◆ Dye 1 ■ Dye 2

Surfactant 2

$y = 0.1343x + 0.0714$

$y = 0.1276x + 0.0389$

◆ Dye 1 ■ Dye 2

Figure 3: Dissolution of dyes in different concentrations of surfactants (0.1%, 0.5% and 1%) at 25$^{°}$C, measured in

C_{dye}=0.2 g/L.

Figure 4 shows the temperature effect on dissolution of dyes in water containing both surfactants. The amount of solubilized dyes increased at higher temperatures. It can be attributed to the enhancement of dye solubilization in surfactant solutions according to Arrhenius-type equation [27].
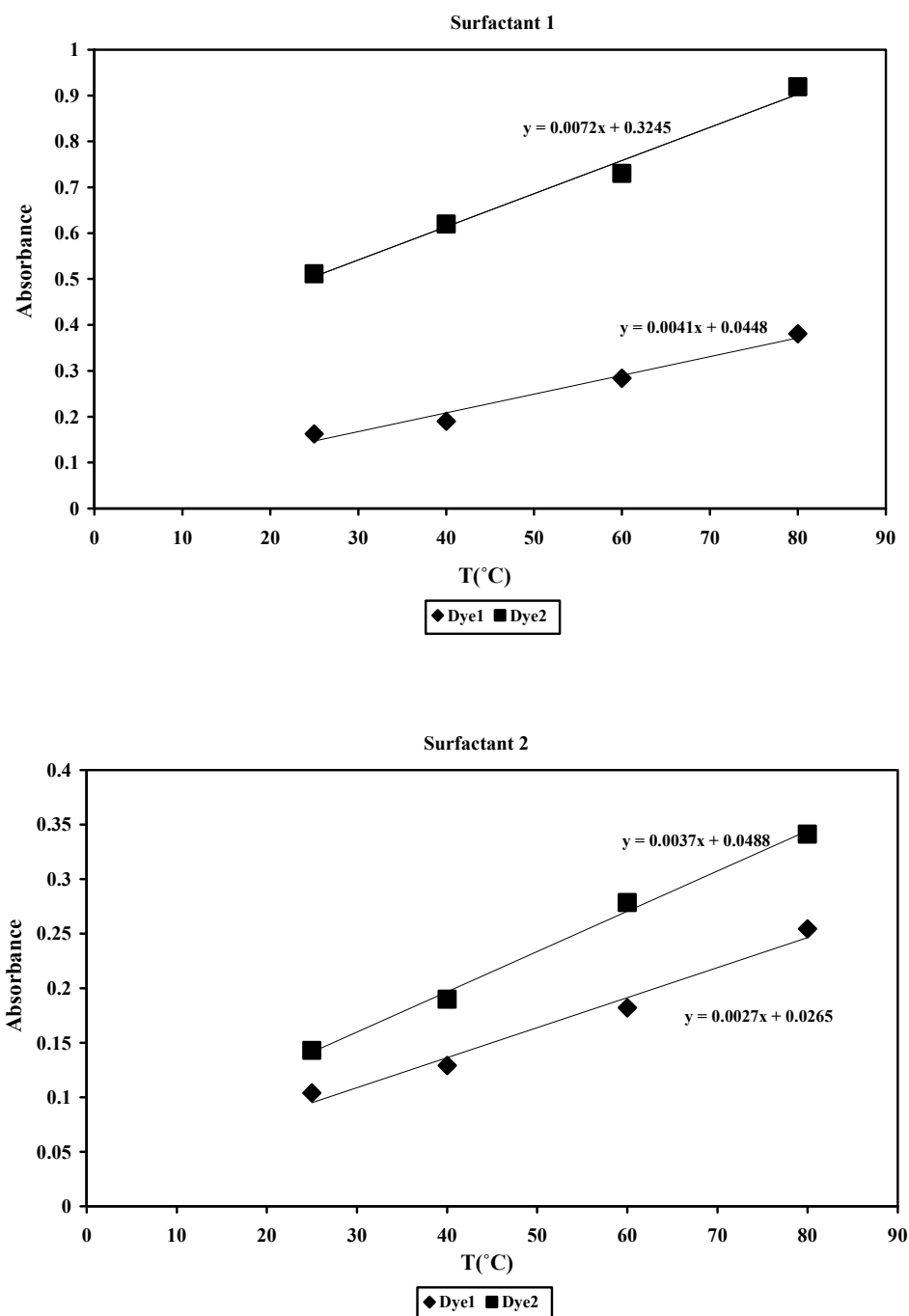
Figure 4: Dissolution of dyes in the presence of surfactants at different tempratures; at 25, 40, 60 and 80° C for 90 minutes, measured in C_{dye}=0.066.

Dissolution of dyes in surfactants increased with time and concentration of the surfactants. It is obvious that in lower concentrations (i.e. < CMC), the dye molecules aggregated, while, in higher concentrations of surfactant (i.e.> CMC), dye exists as single molecules. By increasing the concentration of the surfactants, the dissolution of these two dyes in water containing both surfactants enhances. The Interactions of the dye molecule and surfactants are more important in solubility of dyes in water than dispersing agents. However, the mechanism and the nature of the interactions between dyes and dispersing agents are clearly understood [28]. Generally, electrostatic and hydrophobic interactions increase the dissolution of dyes in water. Micelle formation in surfactant solution is induced by the hydrophobic interactions between hydrocarbon groups of the dispersing agent molecules balanced by their hydration and electrostatic repulsive effects [28]. Disperse dyes exist as aggregated particles in water and dispersing agents reduce or eliminate the aggregations in the micelles.

3.1. Dissolution rate of dyes in surfactant solutions

The current concentration of dissolved dyes in additive-containing water obtains from equation 1[24, 25].
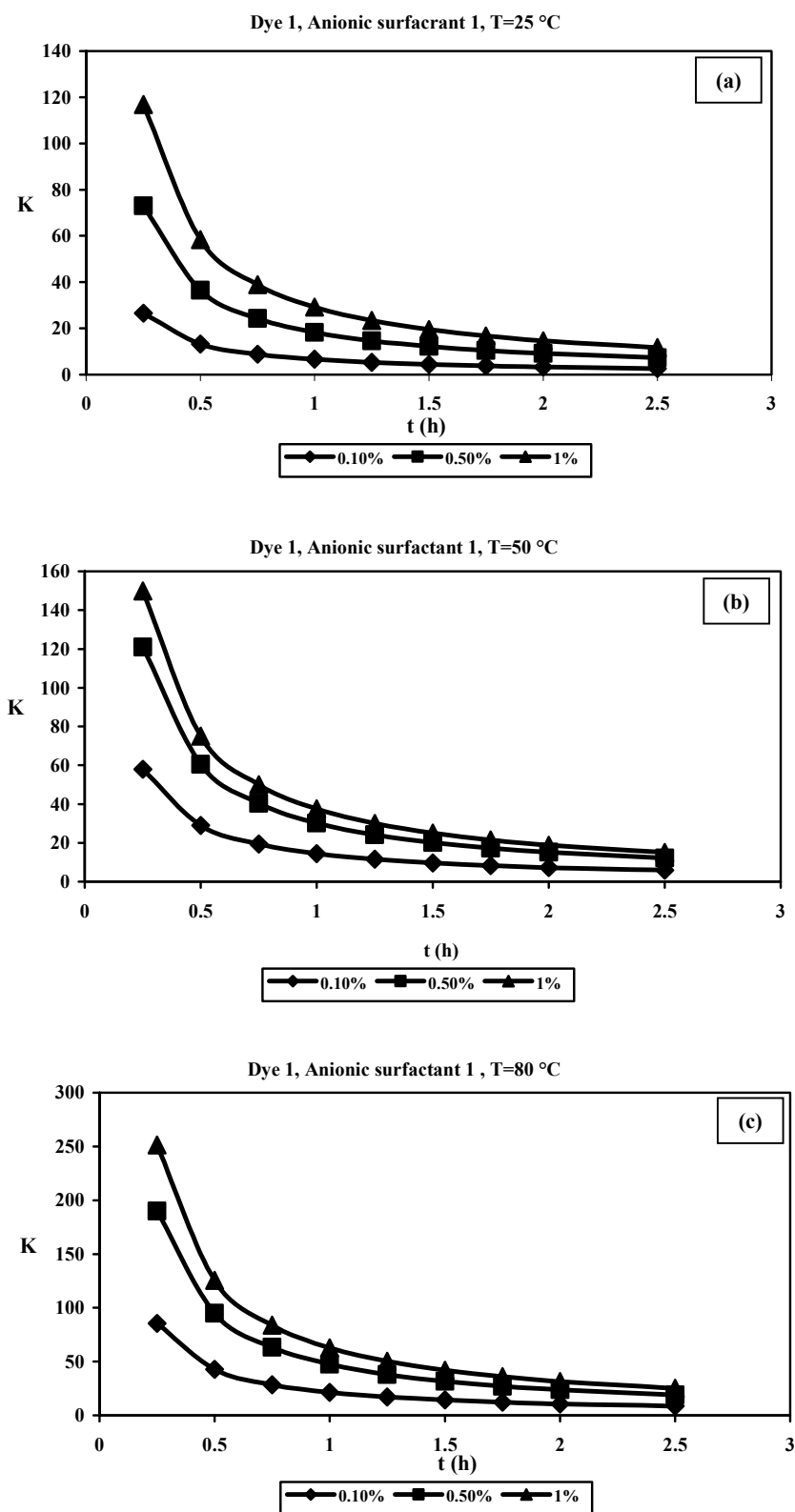
$$C = \kappa \ln k' / \kappa + \kappa \ln t \qquad (1)$$

where k is the rate constant, k′ is proportional to the rate constant, κ is proportional to dye solubility, C is the current concentration of the solute and t is time.

In this work, we considered dissolution rate of two monoazo dyes derived from naphthalimide ring containing carboxylic acid group in the presence of formaldehyde condensation of naphthalenesulphonic acid and fatty alcohol ethylene oxide at 25, 50 and 80°C. Figures 5, 6 and Table 1 demonstrate that dissolution rate of both dyes in the presence of surfactants at different conditions is in accordance with equation 1 ($r^2 \geq 0.96$).

Table 1: The constant rate of dye dissolution in water containing various surfactants at different temperatures and various concentrations.

Dye	Surfactant	Concentration	25°C		50°C		80°C	
			κ (10^{-3})	r^2	κ (10^{-3})	r^2	κ (10^{-3})	r^2
1	1	0.1%	6.63	0.98	14.49	0.97	21.35	0.97
		0.5%	18.25	0.99	30.23	0.96	47.50	0.96
		1%	29.20	0.97	37.50	0.99	62.87	0.99
	2	0.1%	2.91	0.98	3.69	0.99	4.74	0.98
		0.5%	5.66	0.97	9.34	0.98	14.77	0.97
		1%	9.80	0.96	14.26	0.96	18.74	0.99
2	1	0.1%	31.06	0.99	33.28	0.98	37.27	0.98
		0.5%	54.86	0.98	66.63	0.98	82.32	0.99
		1%	86.51	0.98	96.52	0.96	108.36	0.97
	2	0.1%	6.16	0.99	9.47	0.97	10.85	0.96
		0.5%	9.43	0.99	26.19	0.98	28.64	0.97
		1%	13.86	0.98	33.60	0.97	33.22	0.99

Dye 1, Anionic surfacrant 1, T=25 °C

Dye 1, Anionic surfactant 1, T=50 °C

Dye 1, Anionic surfactant 1 , T=80 °C

Figure 5: Dissolution rate of dye1 in surfactant solutions at different temperatures and various surfactant concentrations; (a) Surfactant 1 at 25°C, (b) at 50°C and (c) at 80°C, and (a′) Surfactant 2 at 25°C, (b′) at 50°C and (c′) at 80°C.

Dye 1, Nonionic surfactant, T=25

Dye 1, Nonionic surfactant, T=50
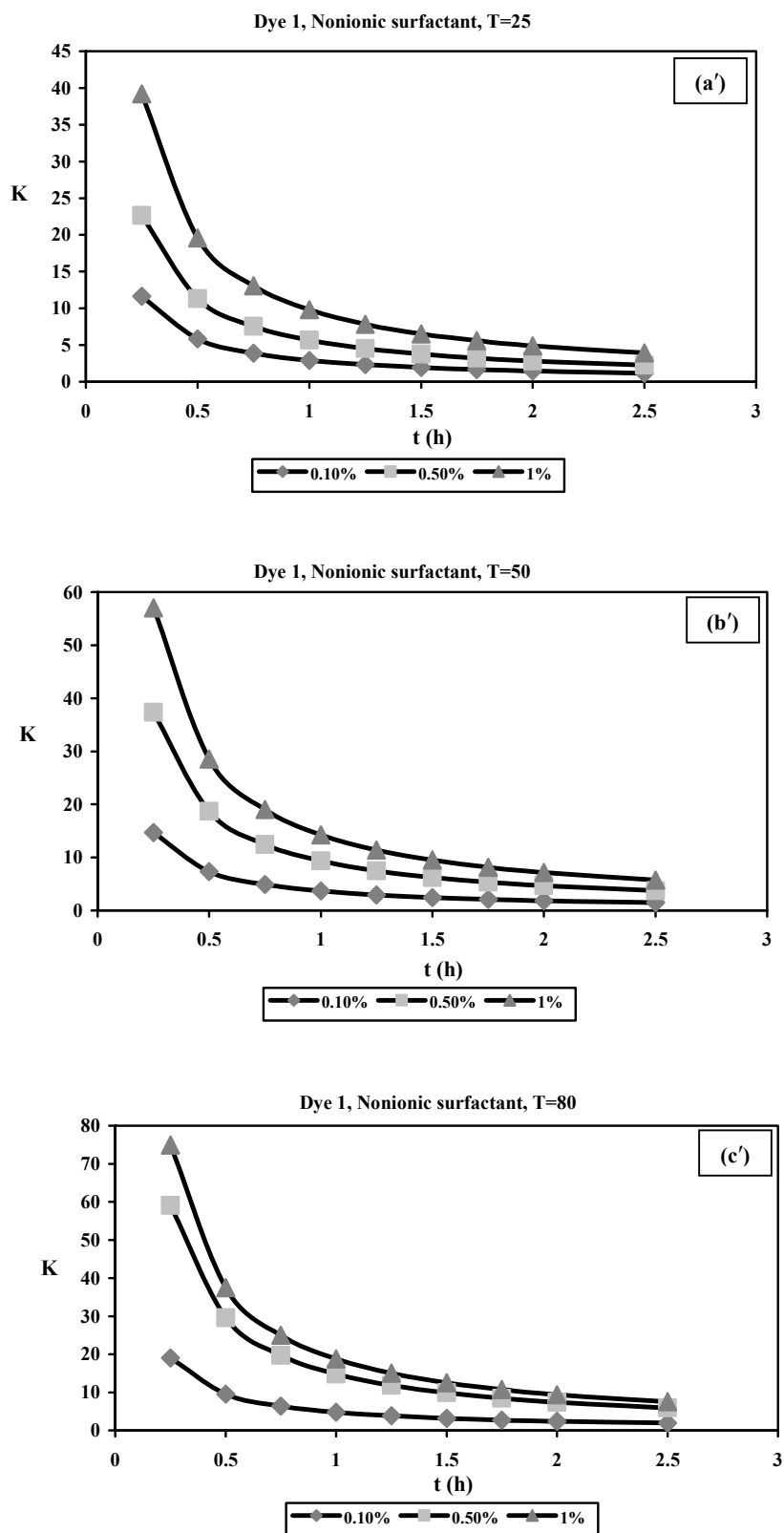
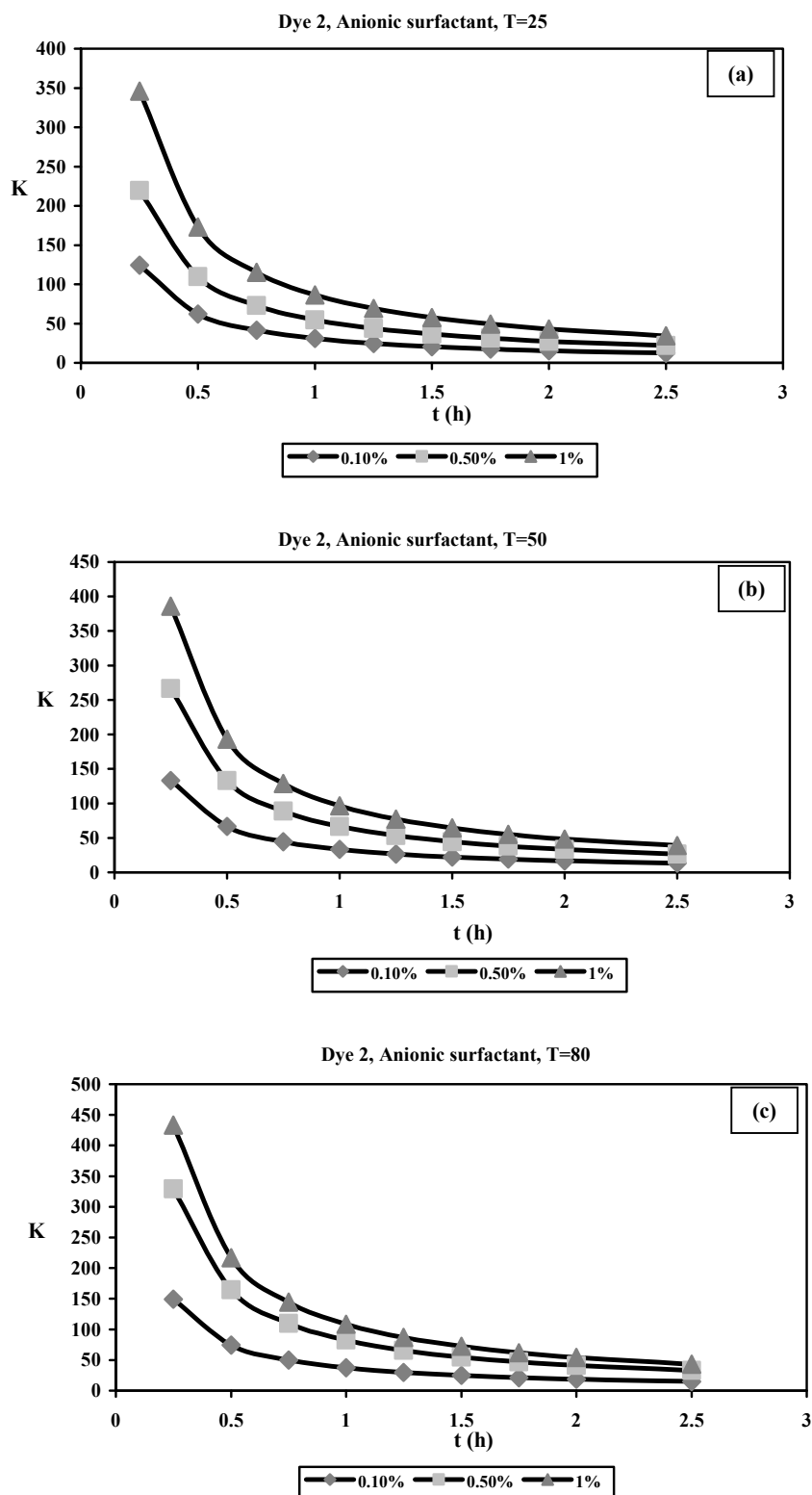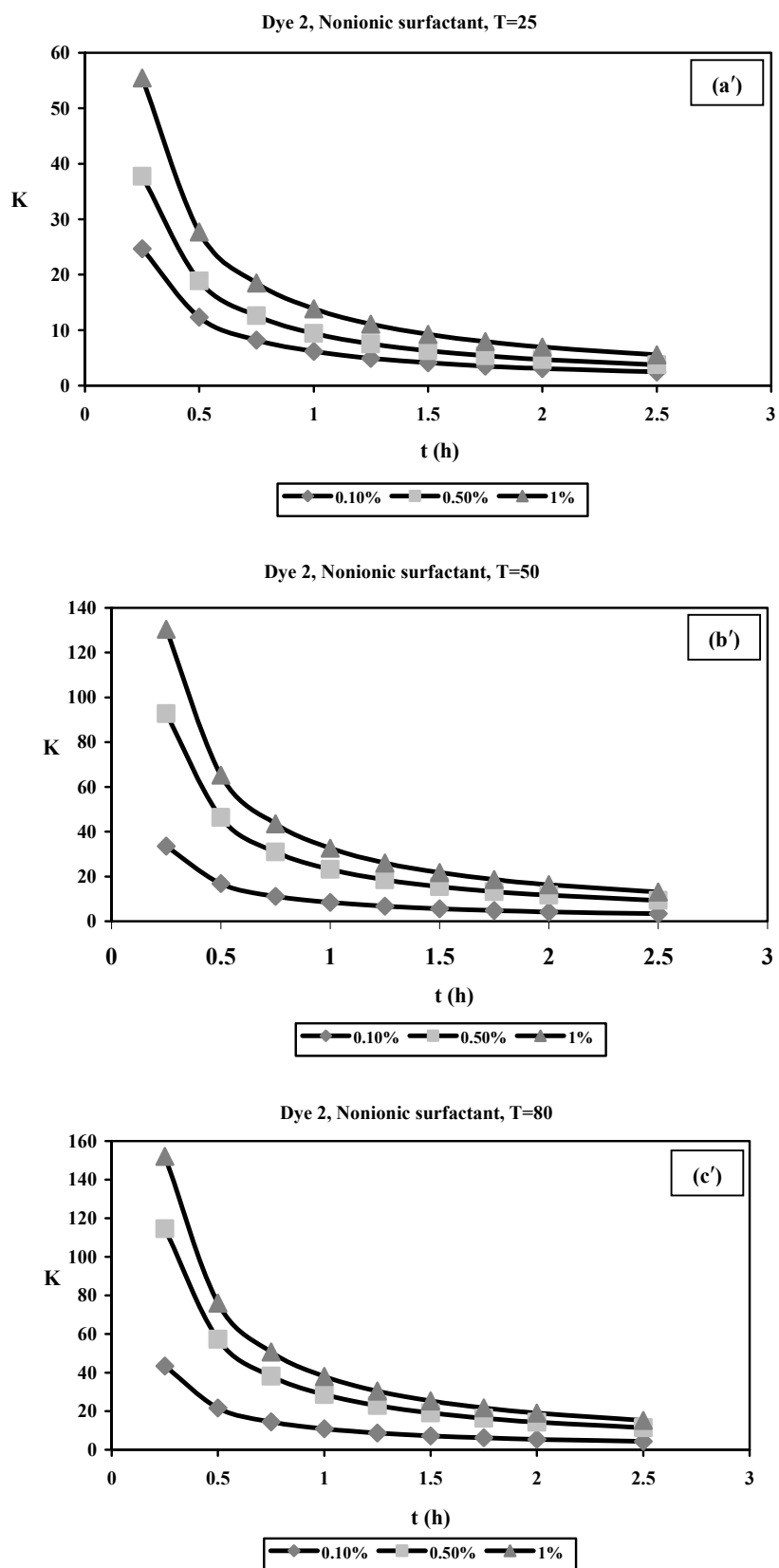**Dye 1, Nonionic surfactant, T=80**

Figure 5: Continued.

Figure 6: Dissolution rate of dye 2 in surfactant solutions at different temperatures and various surfactant concentrations; a: Surfactant 1 at 25°C, b: at 50°C and c; at 80°C; a′: Surfactant 2 at 25°C, b′: at 50°C and c′: at 80°C.

Dye 2, Nonionic surfactant, T=25

(a′)

Dye 2, Nonionic surfactant, T=50

(b′)

Dye 2, Nonionic surfactant, T=80

(c′)

Figure 6: Continued.

Results revealed that in all cases, the dye solubility (κ) increased with increasing the surfactant concentration in the media and the process temperature (Table 1). However, the solubility of both dyes in water containing surfactant 1was higher than surfactant 2. In addition, dye 2 had better solubility relative to dye 1 in surfactant solutions. The high solubility rate constants of dye 2 relative to dye 1 can be ascribed to its chemical structure. Dye 2 has an additional hydroxyl group in its chemical structure and it has higher solubility in surfactant micelle solution. The lowest and highest solubility constant of dyes in the presence of various surfactants occurred at 25°C and 80°C, respectively.

Disperse dyes generally have an extremely low solubility (0.1-100 mg/l), which increases proportional to the temperature. There is always a balance between dissolved and dispersed states of dyes in the solutions. Increasing the temperature, agitation and addition of some surfactants can increase the amount of dissolved dye in the solutions. The surfactant micelles produce a cover around dye molecules and enhance its solubility and dispersing ability in water. A Dye with high molecular weight has less solubility in water; however, the presence of hydrophilic groups increases its solubility and dispersion capability. This is the case for dye 2 in comparison with dye 1. The surfactant micelles increase the solubility of the dye in water. On the other hands, the presence of hydroxyl group in dye molecule results in the formation of hydrogen bond with water molecules.

In our previous work, the dissolution kinetic of some monoazo disperse dyes based on N-alkyl and N-carboxylic acid naphthalimides in water containing various dispersing agents were investigated. In these studies, the diazo component of 4-amino N-methyl, N-

propyl and N-buthanoic acid-1,8-naphthalimides and N,N-diethyl-m- toluidine and couplers 3-acetamodo-N,N-diethylaniline were used. Results showed that the dissolution kinetic of dyes in the presence of dispersing agents followed an exponential rate equation. Similar results were obtained for the dyes in the current study. However, the dissolution rate of these dyes relative to previous dyes is very high, especially for dye 2. The presence of both carboxylic acid and hydroxyl groups in dye molecule resulted in the increase of dissolution rate; for example, the κ value for dye 2 in the anionic dispersing agent (1%) at 80°C was 108.36×10^{-3}, while the κ value for N-alkyl-1,8-naphthalimide studied in previous work was 12.57×10^{-3} under the same conditions. On the other hand, the presence of hydroxyl group in dye molecule can increase the solubility of the dye in water containing dispersing agents.

4. Conclusions

The effects of different parameters such as temperature, time and surfactant concentration on dissolution of two monoazo napthalimide disperse dyes have been investigated. The solubility of both dyes increased by temperature and surfactant concentration. The solubility kinetic study of dyes in aqueous surfactant solutions suggested that the solubility behavior of all used dyes follows the exponential equation 1 and that the higher rate constant values for dye 2 compared to dye 1 was attributed to one additional hydroxyl group in its chemical structure.

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