

Cationic ester-containing gemini surfactants as retarders in acrylic dyeing



Mousa Sadeghi-Kiakhani^{a,*}, Ali Reza Tehrani-Bagha^b

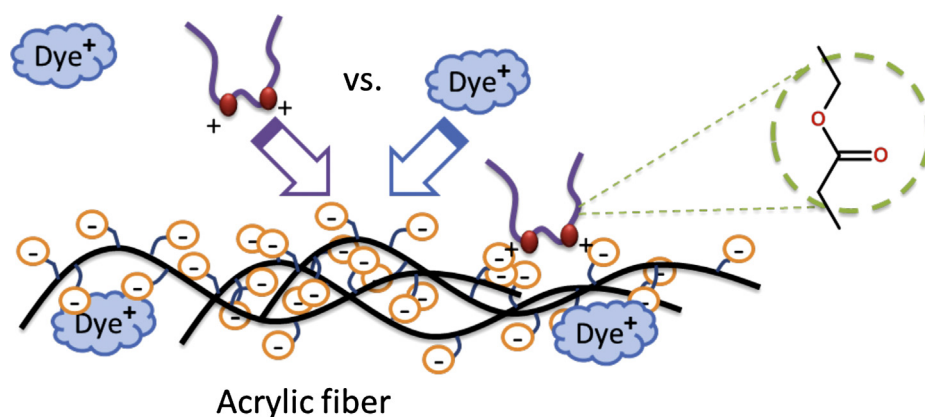
^a Institute for Color Science and Technology, Department of Organic Colorants, Tehran, Iran

^b Department of Chemical and Petroleum Engineering, American University of Beirut (AUB), Beirut, Lebanon

HIGHLIGHTS

- Three cationic gemini surfactants were used as retarders in acrylic dyeing.
- The kinetic of acrylic dyeing was studied using various empirical models.
- The surfactants reduced the rate of cationic dye adsorption.
- The rate of dye adsorption was increased by temperature.
- The ester-containing geminis showed much weaker blocking effect.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 December 2014

Received in revised form 20 March 2015

Accepted 24 March 2015

Available online 1 April 2015

Keywords:

Gemini cationic surfactant

Ester bond

Acrylic dyeing

Dye adsorption

Cationic dye

ABSTRACT

Two ester-containing cationic gemini surfactants (esterquat and betainester types) and one stable cationic gemini surfactant with the same spacer length between the two quaternary head groups were investigated as retarding agents in acrylic dyeing with a cationic dye. The effects of surfactant concentration, time, and temperature were studied on cationic dye adsorption onto acrylic fibers. The results indicated that the presence of ester bond in alkyl tails of cationic gemini surfactants has an important role on the retarding action of dyeing process and it reduces the blocking effect. The dye adsorption kinetic at various surfactant concentrations and temperatures was studied by using different empirical models. The cationic dye adsorption on acrylic fiber showed a very good correlation with the modified Cegarra-Puente empirical model. According to the obtained activation energy values, the dye diffusion into the fiber depends significantly on the chemical structure of the used gemini cationic surfactants and their concentrations.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Acrylic fiber is one of the most popular synthetic fibers and its annual production was ~2.2 million tons/year in 2010 [1,2]. This fiber has extensive applications in apparel as well as in various industrial sectors owing to its outstanding physical and chemical properties such as high strength and good abrasion and insect

* Corresponding author. Tel.: +98 21 22969774; fax: +98 21 22969774.
E-mail address: sadeghi-mo@icrc.ac.ir (M. Sadeghi-Kiakhani).

resistance. Due to the importance of acrylic fibers in textile industry, investigation for improving their dyeing properties is still very interesting. Acrylic fibers consist of at least 85% acrylonitrile monomer and typical co-monomers are vinyl acetate or methyl acrylate which makes the fiber dyeable by cationic dyes [3–5].

The cationic dyes used for dyeing anionically modified polyacrylonitrile fibers usually adsorb very rapidly into the fiber at above the glass transition temperature (T_g). Due to very strong ion-exchange interaction between the cationic dyes and anionic dye sites on the polymer surface, the dye adsorption is very fast and irreversible to a large extent. To overcome this problem, the temperature control and/or electrolyte addition are usually inadequate for achieving a uniform dye adsorption on the fiber (i.e. level dyeing) [6–8]. Therefore, the use of surfactants as leveling agents (known as retarders in textile terminology) is strongly recommended in acrylic dyeing. Colorless leveling agents (mostly cationic surfactants) compete with cationic dyes to adsorb at limited oppositely charged dye-sites on the fiber surface and within the interior of the acrylic fiber. This dynamic competitive adsorption reduces the adsorption rate of cationic dyes, and leads to uniform distribution of dye molecules at the fiber surface [9–11]. This topic has been studied in a number of scientific papers and it has been found that the structure of surfactants and their concentrations are the main effective factors to control the dye adsorption rate [12–14].

Gemini surfactants are among new generation of surfactants composed of two hydrophobic tails and two hydrophilic head groups which are bonded together by a chemical linkage. The variables in their chemical structures can be the length, polarity, and rigidity of the alkyl tails and the linkage/spacer. Most of their interesting physical chemical properties are related somehow to their higher surface activity and lower critical micelle concentration (CMC) values [15–17]. A much smaller amount of a gemini surfactant is required to perform the same function compared with that of a monomeric counterpart and this offers the possibility of decreasing the environmental impact of formulations [18–20]. A series of stable cationic gemini surfactants with various spacers and alkyl tail lengths was tested as retarders in acrylic dyeing and compared with a single chain cationic surfactant, dodecyltrimethylammonium bromide (DTAB) [12]. They were found to be much more efficient than DTAB in reducing the rate of dye adsorption (i.e. as retarders). However, the biodegradation results showed that the stable cationic gemini surfactants are toxic and not readily biodegradable. To overcome this problem, we have followed the concept of adding a cleavable bond (i.e. ester bond) in the chemical structure of these cationic surfactants. The physical and chemical properties of cationic ester-containing gemini surfactants have been previously studied in a series of papers [21–29]. Two types of such amphiphiles have been investigated, one with the ether oxygen of the ester bond turned toward the quaternary ammonium group (known as betain-ester type) and one with the reverse orientation of the ester bond (known as esterquat type) [22,23,29].

The purpose of this study is to investigate the performance of cationic ester-containing gemini surfactants as retarders in acrylic dyeing with a cationic dye. The results are compared with those of a stable cationic gemini surfactant with the same spacer length. Furthermore, a series of empirical kinetic models is employed to fit the kinetic of acrylic dyeing in order to have a better comparison between the investigated surfactants.

2. Experimental

2.1. Materials and equipment

N,N-dimethyldodecylamine (97%), 1,3-dibromopropane (99%), 2-dimethylaminoethanol (>99.5%), decanoyl chloride (98%), acetone (>99.5), ethanol (99.5%), diethyl ether (99%), magnesium

sulfate (>99%) and sodium hydrogen carbonate (>99%) were all purchased from Aldrich.

High bulk acrylic yarn 24/2 Nm type was used after normal washing and drying procedure. C.I. Basic Blue 41 (BB41) was purchased from Dystar Co. and used without further purification. The UV-Visible absorption spectra of dyes in the solution of surfactants were measured by Cecil 9200 double beam spectrophotometer. A CDM 210 conductometer (Radiometer) was used to measure the CMC values of the surfactants. An Infrared sample dyeing machine (India) was employed for acrylic dyeing.

2.2. Synthesis of surfactants

The details of synthesis of the surfactants have been reported in our previous papers [23,25,31]. Schematic presentation of the synthesis methods is provided in Scheme 1.

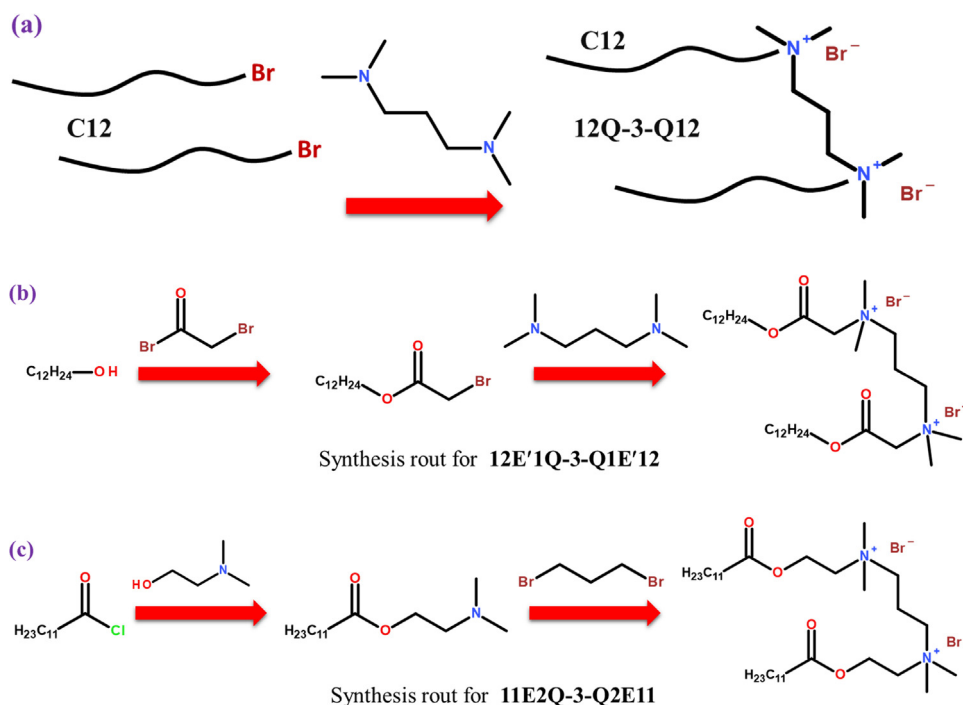
2.3. Conductometry measurements for CMC determination

The plot of specific conductivity versus concentration of an ionic surfactant solution can be used to determine the critical micelle concentration (CMC) of the surfactant. By increasing the concentration of surfactant in solution, the conductivity increases linearly. There is a break and change in the slope of increment at CMC as a result of counterion binding to the formed micelles. The measurements were performed with a CDM 210 conductometer (Radiometer) in a temperature-controlled double walled glass container with water circulation. For each series of measurements, an exact volume of 10 ml Millipore water (resistivity $\sim 18 \text{ M}\Omega$) was introduced into the vessel. The solution was then titrated with the surfactant solution with known concentration and the specific conductivity was measured every 2–3 min after each addition.

2.4. Acrylic dyeing

In acrylic dyeing by cationic dyes, every acrylic fiber shows a finite saturation value associated with the anionic sites in the fiber. The saturation concentration (C_s) of BB41 on the acrylic fiber was obtained to be 6% (over weight of fiber) based on the standard test procedure [30]. This value is very important for practical dyeing of acrylic fiber and is the dye concentration at which 90% exhaustion on to the fiber is achieved. The initial dye concentration was set at 1.5% (o.w.f.) (i.e. one quarter of the saturation concentration) for the rest of the dyeing experiments. Therefore, the initial dye concentration would be always lower than the amount needed to interact with all available oppositely charged dye-sites on the fiber which results in fast dye adsorption on to fiber at above T_g temperature.

The pH of the dye-bath was adjusted to 4.5 by using 1% (o.w.f.) acetic acid (glacial) and 1% (o.w.f.) sodium acetate crystals. The liquor to acrylic fiber ratio was adjusted to 50:1 by adding distilled water. This liquor to fiber ratio has also been used in the standard test method for determination of saturation characteristics of dye and other kinetic studies [29]. The dye adsorption study was investigated at three different temperatures (i.e. 90, 95 and 100 °C), and at various surfactant to dye molar ratios. The dyeing procedure was carried out using an Infrared sample dyeing machine. For monitoring the kinetic of dye adsorption, 12 acrylic samples (each 1 g) were dyed simultaneously in 12 different steel cylinders containing the prepared dye solution. After reaching to set temperature and at various time intervals (i.e. 5, 10, 15, 20, 30, 60, 90 and 120 min), one cylinder was removed from the dyeing machine and quenched by fast cooling under the tap water. The dyed samples were then removed from each dye-bath immediately to stop the dyeing procedure. It should be noted that the dye adsorption on acrylic fiber stops at temperature below the T_g of the fiber (around 80–85 °C). The absorbance of the dye solution, after certain



Scheme 1. Synthesis rout for (a) stable gemini surfactant 12Q-3-Q12, (b) dodecyl betainester gemini 12E'1Q-3-Q1E'12, and (c) dodecylesterquat 11E2Q-3-Q2E11. In these nomenclatures, Q represents quaternary ammonium group, E stands for ester bond (Esterquat type), E' stands for ester bond in reverse order (Betainester type) and the numbers indicate the carbon atoms in methylene chain.

dilution, was measured at λ_{\max} of BB41 (605 nm) before and after the dyeing process using a UV-Vis spectrophotometer. The percentage of dye adsorption onto acrylic sample was calculated using Eq. (1):

$$\text{Dye adsorption \%} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where C_0 is the initial dye concentration and C_t is the dye concentration at time t after reaching to the set temperature.

It is important to note that no change is observed in the visible spectra of cationic dye solution in the presence of different concentrations of cationic surfactants which shows that there is not any apparent interaction between the cationic dye and the cationic surfactants in the solution.

2.5. Pretreatment effect

Acrylic samples were first pretreated in surfactant solutions 2% (o.w.f) individually at 100 °C for 2 h and the samples were rinsed thoroughly and dried. The dye adsorption onto these pretreated samples was investigated in the same way as described in Section 2.4. This was to determine the ability of dye molecules to replace the pre-adsorbed surfactant molecules onto the acrylic fiber.

In addition, the effect of the cationic surfactants on desorption of the cationic dye from pre-dyed fibers was determined. The dyed samples were placed in the surfactant solution 1% (o.w.f) and treated at 100 °C for 2 h. At the end of this procedure, the amount of desorbed dye into the dye-bath solution was determined using UV-Vis spectroscopy.

2.6. Empirical kinetic models

The empirical kinetic models can be used to estimate the dyeing rate constant which shows how fast the dye adsorption takes place. There are a number of empirical kinetic models for determination of

the rate constant (k) such the zero order or parabolic equation (Eq. (2)), the first order or exponential equation (Eq. (3)), the Cegarra and Puente equation (Eq. (4)) and the modified Cegarra-Puente equation (Eq. (5)) [14,30].

$$\frac{dC_t}{dt} = \frac{k}{C_t} \rightarrow C_t = k\sqrt{t} \quad (2)$$

$$\frac{dC_t}{dt} = k(C_\infty - C_t) \rightarrow \ln\left(1 - \frac{C_t}{C_\infty}\right) = -kt \quad (3)$$

$$\ln\left(1 - \frac{C_t^2}{C_\infty^2}\right) = -kt \quad (4)$$

$$\ln\left[-\ln\left(1 - \frac{C_t^2}{C_\infty^2}\right)\right] = a \times \ln k + a \times \ln t \quad (5)$$

2.7. Activation energy

Apparent activation energy in the dyeing process (E_a) can be calculated from the empirical Arrhenius equation (Eq. (6)) [32]:

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (6)$$

where k is the rate constant; R the gas constant (8.314 J/mol K), and T the absolute temperature (K), and E_a is apparent activation energy of adsorption (J/mol). Plotting the rate of adsorption against the reciprocal temperature gives a reasonably straight line, the gradient of which is $-E_a/R$.

3. Results and discussion

3.1. Syntheses and physical-chemical properties of the surfactants

The synthesis of cationic gemini surfactants can be followed by two different methods as can be seen in Scheme 1. In the first method, (Scheme 1-a and b), the target geminis (12Q-3-Q12 and 12E'1Q-3-Q1E'12) with short spacer ($s=3$) are

synthesized from the reaction of the corresponding alkyl bromide with *N,N,N',N'*-tetramethyl-1,3-diaminopropane. For synthesis of *Dodecyl bromoacetate* (i.e. the intermediate product in Scheme 1-b), one may react 1-dodecanol with Bromoacetyl bromide in dichloromethane [29]. In the second method (Scheme 1-c) which is more common in synthesis of cationic gemini surfactants with long spacer ($s > 3$), the gemini is obtained from the reaction of corresponding fatty tertiary amine with 1,3-dibromopropane. The fatty tertiary amine in this work (i.e. *N*-(2-(dodecanoyloxy)ethyl)-*N,N*-dimethylamine) was synthesized by reaction of 2-(*N,N*-dimethyl)aminoethanol and lauroyl chloride as previously described in details elsewhere [24,25,29].

The CMC values of the surfactants were measured by conductometry method (Section 2.3). The CMC values of 12Q-3-Q12, 12E'1Q-3-Q1E'12, and 11E2Q-3-Q2E11 were found to be 0.99 mM, 0.24 mM, and 0.31 mM, respectively at 25 °C. The CMC values of the ester-containing surfactants are very close to each other as a result of similar alkyl tail length and chemical structure. These CMC values are 3–4 times smaller than the CMC value of 12Q-3-Q12 as a result of longer alkyl chain length. These CMC values are at least 10 times smaller than those of the corresponding single chain surfactants [22,23,27], which is favorable from economic and environmental point of view [15].

3.2. Retarding action of surfactants

3.2.1. Surfactant concentration effect

The cationic dye absorption onto acrylic sample at initial dye concentration of 1.5% (o.w.f) and at two different surfactant concentrations (Surfactant: Dye molar ratios = 0.25 and 0.5) was investigated at 100 °C (Fig. 1). The results clearly show that in the absence of any surfactant, the dye absorbs quickly onto acrylic fiber which is the cause of non-uniform dyeing on the samples. By increasing the concentration of the cationic surfactants in the dye bath, the rate of dye absorption decreases substantially. Some retarders are strongly bonded to the oppositely charged dye sites on the fiber in case they are used at high concentrations. A permanent blocking effect can be observed when the stable gemini surfactant (i.e. 12Q-3-Q12) is used while the other two ester-containing geminis have not caused this problem which is beneficial from the dyeing point of view. This suggests that inserting a weak cleavable bond (e.g. ester bond) in the alkyl tail of the surfactants will solve the blocking effect of the retarders. The ester bond in these surfactants is susceptible to chemical hydrolysis especially at elevated pH and temperature [30,31]. It has been shown that an ester-containing gemini surfactant has extremely slow chemical hydrolysis in water at pH below 4 [33]. Upon chemical hydrolysis at elevated dyeing temperature, 12E'1Q-3-Q1E'12 breaks into dodecanol and the diquatery-dicarboxylic salt and 11E2Q-3-Q2E11 breaks into dodecnionic acid and the diquatery-diol salt. The resulting degradation products are not able to compete with the cationic dye for adsorption (i.e. they are not retarder anymore) and as a result the ester-containing surfactants do not show any permanent blocking effect in the dyeing process.

The position and direction of the ester bonds in alkyl tails toward the cationic head groups in 12E'1Q-3-Q1E'12 and 11E2Q-3-Q2E11 are also playing a very important role in chemical hydrolysis as it has been mentioned in other papers [12,29]. Compared with 11E2Q-3-Q2E11, 12E'1Q-3-Q1E'12 is susceptible to faster chemical hydrolysis. The cationic head groups withdraw electron from the carbon of carbonyl group and make it more prone to nucleophilic attacks. Obviously, the carbon of carbonyl group is closer to the cationic head groups in 12E'1Q-3-Q1E'12 than in 11E2Q-3-Q2E11 which results in faster chemical hydrolysis in alkaline and mild acidic condition.

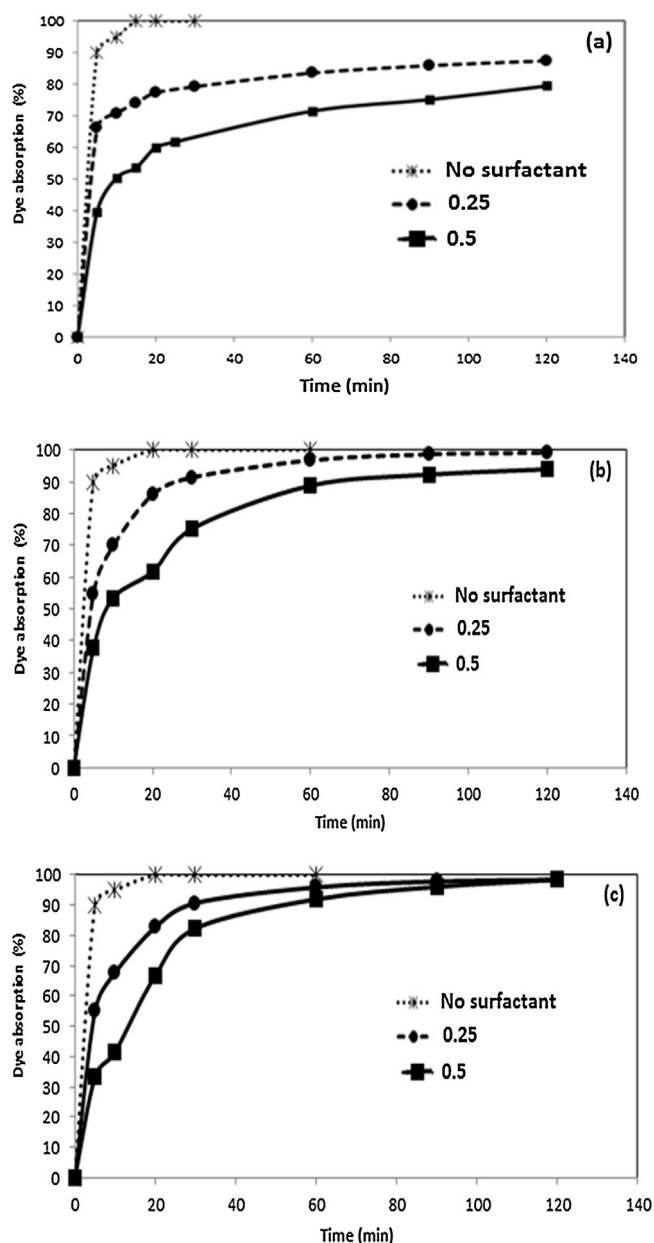


Fig. 1. BB41 absorption (%) onto acrylic fiber in the presence of the gemini surfactants at (Surfactant: Dye molar ratios = 0.25 and 0.5) at 100 °C (a) 12Q-3-Q12, (b) 11E2Q-3-Q2E11, and (c) 12E'1Q-3-Q1E'12.

The mechanism of dyeing of acrylic fibers with cationic dyes involves electrostatic interaction between the anionic sites on the fiber and the dye cations. This electrostatic interaction can be reinforced further by the hydrophobic interaction between the aromatic part of the dye cation and the methylene chains in acrylic polymer. Acrylic dyeing can take place by an ion-exchange process in which the dye cations adsorb at the surface of the fiber and displace smaller inorganic cations such as the sodium ions which are often attached to the anionic sites of the fiber. The availability of anionic dye sites increases dramatically by increasing the temperature above the T_g of the acrylic fiber [9–11].

The dye cations are adsorbed initially on the fiber surface. In the next step, they should diffuse into the interior of the fiber. Any significant diffusion is possible only by the freeing of the dye molecules from their local interactions with the polymer. This is affected by elevating the temperature of the dyebath which increases the polymeric chain motions and reduces the packing obstruction against

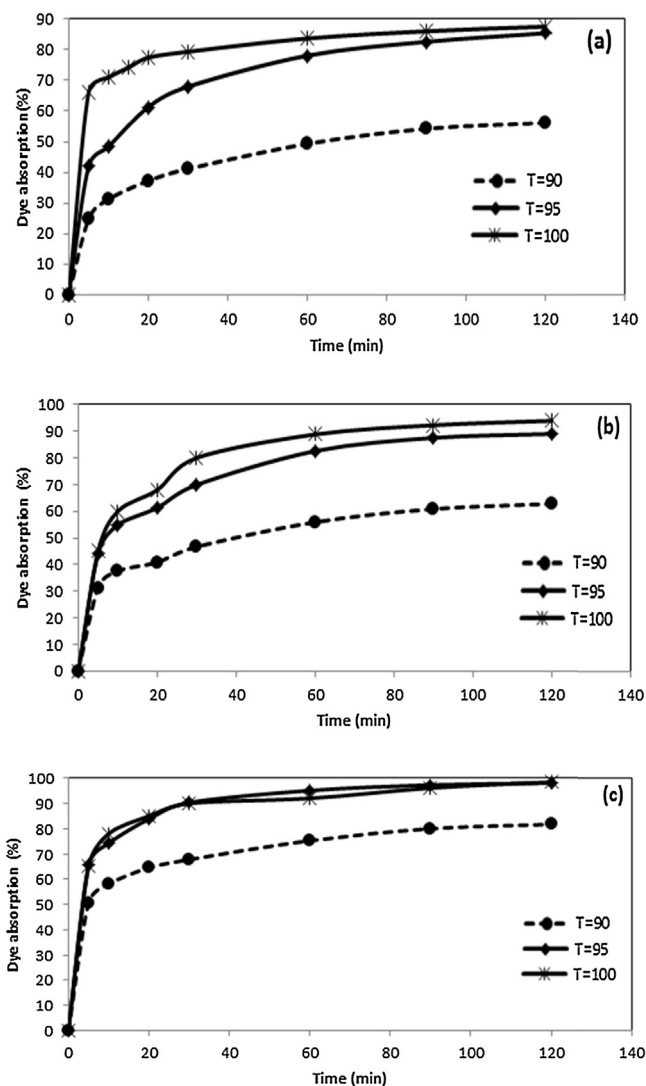


Fig. 2. BB41 absorption (%) onto acrylic fiber in the presence of geminis (Surfactant: Dye molar ratio = 0.5) at different temperatures; (a) 12Q-3-Q12, (b) 11E2Q-3-Q2E11, and (c) 12E'1Q-3-Q1E'12.

diffusion of the dye molecules. These two distinct effects of temperature combine to assist the penetration of dye molecules into the fiber [9–11].

In case the dye adsorption onto the fiber is not uniform, it would be very difficult to fix the problem as a result of strong electrostatic interaction of the dye molecules with oppositely charged dye sites and low migration rate. Thus, it is very important to control the rate of dye adsorption from very early stages in the dyeing process by using suitable retarders.

Fig. 2 shows that the rate of dye adsorption is very high and the complete dye adsorption is achieved in about 10 min which increases the risk of unlevel dyeing (i.e. non-uniform distribution of dye molecules at the fiber surface). The presence of cationic surfactants as retarders has decreased the rate of dyeing and delayed the time needed for the complete dye adsorption.

The effect of different gemini surfactants on the dye absorption (%) at the same surfactant: dye molar concentration was studied at different temperatures (Fig. 2). The plots clearly show the effect of temperature on dye adsorption and the rate of dyeing. As previously explained, the segmental motion of the polymer chains increases exponentially at temperature higher than T_g and more cationic dyes/surfactants can diffuse and adsorb at oppositely

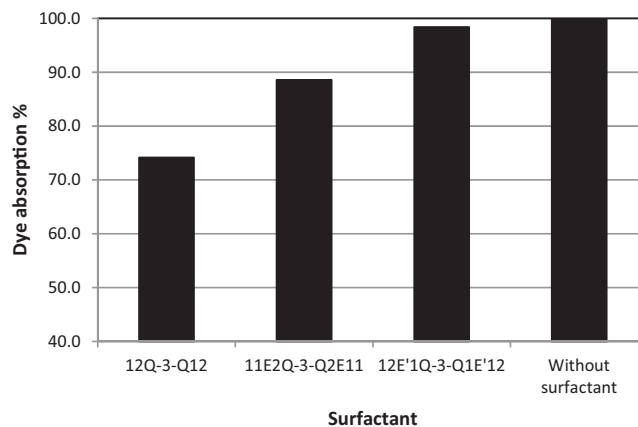


Fig. 3. Dye absorption (%) of cationic dye onto pretreated acrylic fiber at 100 °C after 2 h.

charged dye-sites on and within the fiber. Thus, the dye adsorption rate will increase considerably with increasing temperature.

There is a slightly different trend in the dye adsorption plots vs. time as can be seen in Fig. 2(a) & (b) and (c). By considering the same dyeing conditions (e.g. same amount of acrylic fiber, cationic dye, temperature, and time), the only effective parameter on dyeing rate of absorption on acrylic fiber is the type of retarder. The betainester type gemini surfactant (12E'1Q-3-Q1E'12) with lower chemical stability seems to have a weaker retarding effect among the geminis. The only way we can explain the differences in rate of dye adsorption on acrylic fiber is that the ester bond in the ester-containing gemini surfactants gradually hydrolyzes during the dyeing process at high temperature. As a result, the surfactant loses its stability and it can not compete with the stable cationic dye in the dye bath.

The ester-containing gemini surfactants have an ester bond in each of their alkyl tails close to the cationic head groups. The presence of the ester bond can also affect the charge density on the polar head group of the surfactants. It is reasonable to assume that the charge density of the polar head groups in 12Q-3-Q12 is higher than those in the ester-containing gemini surfactants and the surfactant can adsorb faster and bond stronger with oppositely charged dye sites on acrylic fiber. This can be another explanation for why 12Q-3-Q12 is a stronger retarder in acrylic dyeing than other two ester-containing gemini surfactants [34].

3.3. Migration test

For understanding the effect of pretreatment at concentrated dye or surfactant solution individually on dye migration from the fiber, a series of acrylic samples was prepared as explained in section 2.5. For the first set of experiments, the pretreated acrylic samples in the cationic surfactant solutions at 2% (o.w.f) were dyed at 100 °C (Fig. 3). The dye absorption (%) onto the pretreated acrylic samples shows that the cationic gemini surfactants have blocked some of the anionic dye sites permanently and the cationic dye cannot access to these adsorption sites at temperature as high as 100 °C after 2 h. The order of blocking effect of the surfactants is as 12Q-3-Q12 > 11E2Q-3-Q2E11 > 12E'1Q-3-Q1E'12. Thus, the pretreatment with 12E'1Q-3-Q1E'12 and 11E2Q-3-Q2E11 shows a weaker effect in comparison with that of 12Q-3-Q12. This strong blocking effect shows that the cationic dye molecules cannot replace the adsorbed surfactant molecules at anionic sites of acrylic fiber.

In the second set of experiments, the pre-dyed acrylic samples were treated in the cationic surfactant solutions at 2% (o.w.f) at 100 °C over 2 h (Fig. 4). In absence of any surfactant, almost no dye desorption can be observed. So, prolongation of the dyeing

Table 1

The dyeing rate constants along with their regression coefficients in the acrylic dyeing with BB41 cationic dye in the presence of the gemini surfactants at various Surfactant: Dye molar ratios at 100 °C.

Surfactant	Surfactant: dye molar ratios	Parabolic (Eq. (2))		First order (Eq. (3))		Modified Cegarra-Puente (Eq. (5))	
		<i>k</i>	<i>R</i> ²	<i>k</i>	<i>R</i> ²	<i>k</i>	<i>R</i> ²
12Q-3-Q12	0.25	0.0228	0.919	0.008	0.905	0.0345	0.996
	0.5	0.0411	0.923	0.0084	0.923	0.0088	0.983
12E'1Q-3-Q1E'12	0.25	0.046	0.794	0.0292	0.927	0.055	0.984
	0.5	0.0754	0.857	0.0323	0.980	0.0283	0.980
11E2Q-3-Q2E12	0.25	0.063	0.906	0.027	0.899	0.0440	0.986
	0.5	0.0145	0.941	0.0044	0.867	0.0095	0.981

Table 2

The dyeing rate constants along with their regression coefficients in the acrylic dyeing with BB41 cationic dye in the presence of the gemini surfactants at 0.25 Surfactant: Dye molar ratio at various temperatures.

Surfactant	<i>T</i> (°C)	Parabolic (Eq. (2))		First Order (Eq. (3))		Modified Cegarra-Puente (Eq. (5))	
		<i>k</i>	<i>R</i> ²	<i>k</i>	<i>R</i> ²	<i>k</i>	<i>R</i> ²
12Q-3-Q12	90	0.0356	0.969	0.0045	0.924	0.0016	0.996
	95	0.0035	0.829	0.0173	0.890	0.0140	0.993
	100	0.0228	0.919	0.008	0.905	0.0345	0.996
12E'1Q-3-Q1E'12	90	0.0345	0.953	0.0083	0.936	0.0109	0.997
	95	0.0352	0.849	0.0277	0.924	0.0325	0.995
	100	0.046	0.794	0.0292	0.927	0.055	0.984
11E2Q-3-Q2E12	90	0.0368	0.976	0.0053	0.940	0.0022	0.989
	95	0.0516	0.947	0.0198	0.915	0.0184	0.992
	100	0.063	0.906	0.027	0.899	0.0440	0.986

Table 3

The correlation coefficients values (*R*²) in the acrylic dyeing with BB41 in the different surfactants.

<i>R</i> ²	Parabolic (Eq. (2))	First order (Eq. (3))	Modified Cegarra-Puente (Eq. (5))
Minimum	0.794	0.867	0.98
Average	0.89	0.916	0.985

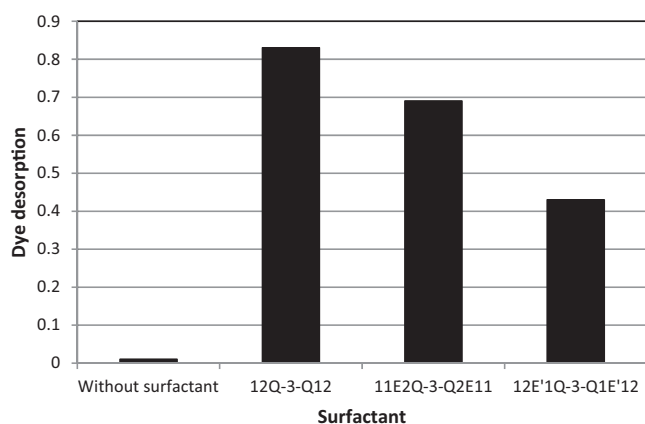


Fig. 4. Dye desorption (optical density) from the pre-dyed acrylic samples in the presence of the cationic gemini surfactants at 2% (o.w.f.) at 100 °C after 2 h.

procedure can not fix the unlevel dyeing and once the dye is adsorbed at fiber surface via ion exchange interaction with anionic dye-sites, it is very difficult to be desorbed. However, the cationic gemini surfactants showed very good ability to replace the adsorbed dye molecules and as a result the dye molecules desorb to the dye bath solution. The effectiveness of the surfactants for causing dye desorption from the fiber to the solution is as: 12Q-3-Q12 > 11E2Q-3-Q2E11 > 12E'1Q-3-Q1E'12 which is in the same order as what it was found for the blocking effect. This shows that the presence of an ester bond in the alkyl tails of the cationic gemini surfactants plays an important role in retarding effect of the

surfactants. This suggests that one may be able to fix the unlevel dyed sample by treating it in cationic surfactant solution at high temperature to facilitate the migration. The suitable surfactant concentration needed for this purpose should be obtained by a series of sample dyeing.

3.4. Kinetic study

A series of kinetic models as described in section 2.6 was employed to study the dyeing kinetic process on acrylic fiber and the rate constants were determined accordingly. In the light of the results obtained, the effect of the cationic gemini surfactants on the rate of dye absorption is reported in Tables 1 and 2. Fifteen different dyeing systems were studied by these models and it was found that the modified Cegarra-Puente empirical model (Eq. (5)) fits the dyeing process somewhat better than the other models.

The mean and minimum correlation coefficients of the all 15 experiments are reported in Table 3 for comparison. It should be noted that the correlation coefficients were also calculated for the other kinetic equations (e.g. parabolic, second order, etc.), but these equations did not show good fitting with the experimental data.

As it can be seen in Table 3, the dyeing kinetic can be described by the modified Cegarra-Puente empirical model somewhat better than the other kinetic models that were used and the minimum and average of the correlation coefficients were found to be 0.98 and 0.985, respectively which were much higher than those of other models. The rate constants obtained from the modified Cegarra-Puente model are depicted vs. temperature for the three cationic gemini surfactants (Fig. 5). This figure clearly shows that the dyeing rate constants increase almost linearly by increasing the

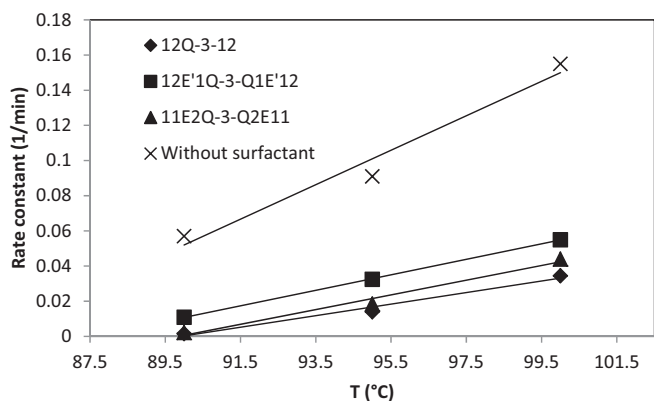


Fig. 5. Dyeing rate constants of BB41 in the presence of the gemini surfactants at different temperatures using Eq. (5).

Table 4

The activation energy in acrylic dyeing process in the presence of gemini cationic surfactants.

Surfactant	E_a (kJ/mol)	R^2
No-surfactant	112.57	0.989
12Q-3-Q12	344.44	0.949
11E2Q-3-Q2E11	337.84	0.948
12E'1Q-3-Q1E'12	182.48	0.963

temperature and in the absence of any retarder; the dyeing rate constants are quite high. By addition of the gemini cationic surfactants as retarders, the dyeing rate constants decrease to a large extent and this is more pronounced than the effect of the temperature. The values of dyeing rate constants in the presence of the gemini cationic surfactants are very close to each other while the betainester type gemini surfactant shows somewhat weaker retarding effect. The order of the retarding action effectiveness for the gemini surfactants (i.e. lower dyeing rate constant) is as: 12Q-3-Q12 > 11E2Q-3-Q2E11 > 12E'1Q-3-Q1E'12.

3.5. Activation energy

The temperature dependence of dyeing constants is most often represented by an Arrhenius equation (Eq. (6)). The apparent activation energy (E_a) decreases with increasing temperature above T_g . The E_a values of the dyeing systems in the absence and presence of the retarders were calculated and reported in Table 4 (see Section 2.7). The E_a increases greatly in the presence of the retarders; therefore the dye molecules require more energy to overcome the energy barrier caused by the presence of the cationic gemini surfactants. The E_a values are close for 12Q-3-Q12 and 11E2Q-3-Q2E11 while 12E'1Q-3-Q1E'12 has much lower E_a value.

4. Conclusion

The retarding action of cationic gemini surfactants in acrylic dyeing was investigated, and it was found that they are effective for reducing the rate of cationic dye adsorption. There are two concerns regarding the stable cationic gemini surfactants: (a) they are not biodegradable, and (b) they show blocking effect in dyeing process. To overcome these problems, the concept of using a cleavable bond (i.e. ester bond) in the alkyl tail of the gemini surfactants was employed. Two ester-containing cationic gemini surfactants (11E2Q-3-Q2E11 and 12E'1Q-3-Q1E'12) were synthesized and their physical-chemical properties as well as their retarding effect in acrylic dyeing were studied. The results were compared with those of the stable gemini surfactant

(i.e. 12Q-3-Q12). The kinetic of acrylic dyeing process by a commercial cationic dye (BB41) was investigated at different surfactant concentrations and temperatures. It was found that the rate of dyeing process was increased by increasing the dyeing temperature and decreasing the concentration of surfactants. The dyeing kinetic data fitted the empirical modified Cegarra-Puente model. The order of retarding and blocking strength of the surfactants in the dyeing process was as 12Q-3-Q12 > 11E2Q-3-Q2E11 > 12E'1Q-3-Q1E'12 showing that the insertion of an ester bond in alkyl tail of a gemini surfactant not only can improve the biodegradation profile of the surfactants, but also it reduces the blocking effect in acrylic dyeing. Therefore, the proof of concept was successful and the insertion of a cleavable bond in the alkyl tails of the gemini surfactants improved both the biodegradability profile and the retarding blocking effect.

References

- [1] R. David, H. Geoffrey, *The Chemistry and Application of Dyes*, New York and London, 1990.
- [2] M.M. Kamel, H.M. Helmy, H.M. Mashaly, H.H. Kafafy, Ultrasonic assisted dyeing: dyeing of acrylic fabrics C.I. Astrazon Basic Red 5BL 200%, *Ultrasonics Sonochem.* 17 (2010) 92–97.
- [3] W. Beckmann, in: D.M. Nunn (Ed.), *The Dyeing of Synthetic-Polymer and Acetate Fibres*, Dyers Company, 1979.
- [4] R.M. EL-Shishtawy, N.S.E. Ahmed, Anionic coloration of acrylic fiber. Part 1: Efficient pretreatment and dyeing with acid dyes, *Coloration Technol.* 121 (2005) 139–146.
- [5] R.M. EL-Shishtawy, S.H. Nasser, N.S.E. Ahmed, Anionic coloration of acrylic fiber. Part II: Printing with reactive, acid and direct dyes, *Dyes Pigments* 74 (2007) 215–222.
- [6] H.H. Wang, Accessibility of acrylic fiber to basic dye, *J. Appl. Polym. Sci.* 111 (2009) 189–193.
- [7] C. Yu, Y. Chen, Study on dyeing properties of functional acrylic fiber, *J. Macromol. Sci. A: Pure Appl. Chem.* 43 (2006) 1695–1702.
- [8] M. Ma, G. Sun, Antimicrobial cationic dyes. Part 3: simultaneous dyeing and antimicrobial finishing of acrylic fabrics, *Dyes Pigments* 66 (2005) 33–41.
- [9] C.L. Bird, W.S. Boston, *The Theory of Coloration of Textiles*, Dyers Company Publications Trust, London, 1975.
- [10] S.M. Burkinshaw, *Chemical Principles of Synthetic Fibre Dyeing*, Blackie Academic & Professional, Chapman & Hall, 1995.
- [11] A.D. Broadbent, *Basic Principles of Textile Coloration*, The Society of Dyers and Colourist, Bradford, 2001.
- [12] A.R. Tehrani-Bagha, H. Bahrami, B. Movvassagh, M. Arami, S.H. Amirshahi, F.M. Menger, Dynamic adsorption of gemini and conventional cationic surfactants onto polyacrylonitrile, *Colloids Surf. A* 307 (2007) 121–127.
- [13] M. Zeydan, D. Yazici, Improvement of process conditions in acrylic fiber dyeing using gray-based Taguchi-neural network approach, *Neural Comput. Appl.* 25 (2014) 155–170.
- [14] J. Cegarra, P. Puente, J.M. Fiadeiro, Kinetics of dyeing acrylic fibres with cationic dyes in the presence of polyethoxylated amines, *JSDC* 102 (1986) 274.
- [15] F.M. Menger, J.S. Keiper, Gemini surfactants, *Angew. Chem. Int. Ed.* 39 (2000) 1906–1920.
- [16] R. Zana, J. Xia, *Gemini Surfactants*, Marcel Dekker, New York, 2004.
- [17] K. Gharanjig, M. Sadeghi-Kiakhani, A.R. Tehrani-Bagha, A. Khosravi, F.M. Menger, Solubility of two disperse dyes derived from N-alkyl and N-carboxylic acid naphthalimides in the presence of gemini cationic surfactants, *J. Surfact. Deterg.* 14 (2011) 381–389.
- [18] M. Mahdavian, A.R. Tehrani-Bagha, K. Holmberg, Comparison of a cationic gemini surfactant and the corresponding monomeric surfactant for corrosion protection of mild steel in hydrochloric acid, *J. Surfactants Deterg.* 14 (2011) 605–613.
- [19] M. Motamedi, A.R. Tehrani-Bagha, M. Mahdavian, A comparative study on the electrochemical behavior of mild steel in sulfamic acid solution in the presence of monomeric and gemini surfactants, *Electrochim. Acta* 58 (2011) 488–496.
- [20] M. Motamedi, A.R. Tehrani-Bagha, M. Mahdavian, Effect of aging time on corrosion inhibition of cationic surfactant on mild steel in sulfamic acid cleaning solution, *Corros. Sci.* 70 (2013) 46–54.
- [21] A.R. Tehrani-Bagha, K. Holmberg, Cleavable surfactants, *Curr. Opin. Colloid Interf. Sci.* 12 (2007) 81–91.
- [22] A.R. Tehrani-Bagha, K. Holmberg, Cationic ester-containing gemini surfactants: adsorption at tailor-made surfaces monitored by SPR and QCM, *Langmuir* 24 (2008) 6140–6145.
- [23] A.R. Tehrani-Bagha, K. Holmberg, Cationic ester-containing gemini surfactants: physical-chemical properties, *Langmuir* 26 (2010) 9276–9282.
- [24] A.R. Tehrani-Bagha, K. Holmberg, M. Nyden, L. Nordstierna, Micelle growth of cationic gemini surfactants studied by NMR and by time-resolved fluorescence quenching, *J. Colloid Interf. Sci.* 405 (2012) 145–149.
- [25] A.R. Tehrani-Bagha, J. Kärbbratt, J.-E. Löfroth, K. Holmberg, Cationic ester-containing gemini surfactants: determination of aggregation numbers by

- time-resolved fluorescence quenching, *J. Colloid Interf. Sci.* 376 (2012) 126–132.
- [26] A.R. Tehrani-Bagha, H. Nikkar, N.M. Mahmoodi, F.M. Menger, The sorption of cationic dyes onto kaolin: kinetic, isotherm and thermodynamic studies, *Desalination* 266 (2011) 274–280.
- [27] W. Beckmann, Determination of the saturation characteristics of basic dyes and acrylic fibres, *JSDC* 89 (1973) 292–295.
- [28] J. Cegarra, P. Puente, J. Valdeperas, M. Pepio, Kinetic aspects of dye addition in continuous integration dyeing, *JSDC* 105 (1989) 349–355.
- [29] A.R. Tehrani-Bagha, H. Oskarsson, C.G. van Ginkel, K. Holmberg, Cationic ester-containing gemini surfactants: chemical hydrolysis and biodegradation, *J. Colloid Interf. Sci.* 312 (2007) 444–452.
- [30] C. Overkempe, A. Annerling, C.G. vanGinkel, P.C. Thomas, D. Boltersdorf, J. Speelman, Esterquats, in: K. Holmberg (Ed.), *Novel Surfactants: Preparation, Applications, and Biodegradability*, Marcel Dekker, New York, 2003.
- [31] M. Stjern Dahl, D. Lundberg, K. Holmberg, *Cleavable Surfactants*, in: K. Holmberg (Ed.), *Novel Surfactants: Preparation, Applications, and Biodegradability*, Marcel Dekker, New York, 2003.
- [32] S.V. Kanth, R. Venba, G.C. Jayakumar, N.K. Chandrababu, Kinetics of leather dyeing pretreated with enzymes: role of acid protease, *Bioresour. Technol.* 100 (2009) 2430–2435.
- [33] A.R. Tehrani-Bagha, K. Holmberg, C.G. van Ginkel, M. Kean, Cationic gemini surfactants with cleavable spacer: chemical hydrolysis, biodegradation, and toxicity, *J. Colloid Interf. Sci.* 449 (2015) 72–79.
- [34] F.J. Chena, A. Asokan, M.J. Cho, Cytosolic delivery of macromolecules: I. Synthesis and characterization of pH-sensitive acyloxyalkylimidazoles, *Biochim. Biophys. Acta* 1611 (2003) 140–150.