Accepted Manuscript

Retarding action of poly(amidoamine) dendrimers and cationic gemini surfactants in acrylic dyeing

Mousa Sadeghi-Kiakhani, Ali Reza Tehrani-Bagha

PII: S0143-7208(15)00420-9

DOI: 10.1016/j.dyepig.2015.10.037

Reference: DYPI 4984

To appear in: Dyes and Pigments

Received Date: 10 June 2015

Revised Date: 26 September 2015

Accepted Date: 26 October 2015

Please cite this article as: Sadeghi-Kiakhani M, Tehrani-Bagha AR, Retarding action of poly(amidoamine) dendrimers and cationic gemini surfactants in acrylic dyeing, *Dyes and Pigments* (2015), doi: 10.1016/j.dyepig.2015.10.037.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Graphical abstract



Retarding action of poly(amidoamine) dendrimers and cationic gemini surfactants in

acrylic dyeing

Mousa Sadeghi-Kiakhani^{1*} and Ali Reza Tehrani-Bagha²

1: Institute for Color Science and Technology, Department of Organic Colorants, Tehran-

Iran

2: Department of Chemical and Petroleum Engineering, American University of Beirut,

Beirut-Lebanon

Corresponding author: Tel: +98 21 22969774; fax: +98 21 22969774; E-mail: sadeghi-

mo@icrc.ac.ir

Abstract

Two cationic gemini surfactants and two generations of poly(amidoamine) (PAMAM) dendrimers (G=-0.5 and G=0.5) were studied as retarders in acrylic dyeing with a cationic dye. Effects of retarder concentrations, dyeing time, and temperature were investigated by means of UV-Vis spectrophotometry. The results indicated that the dye adsorption decreased in the presence of all species and more uniform dyeing was achieved. The PAMAM dendrimers had lower retarding action than the cationic gemini surfactants which was attributed to their non-permanent and lower cationic charge density. Kinetics of the dyeing systems were also evaluated by four different empirical models. The modified Cegarra-Puente model fitted the dyeing kinetic data somewhat better than the other empirical kinetic models. Moreover, the activation energy of the dyeing systems was calculated and reported.

Keywords: Acrylic dyeing, Dye adsorption, Cationic dye, Poly(amidoamine) dendrimers, Cationic Gemini surfactants.

1. Introduction

Dendrimers are highly branched molecules typically symmetric around a core with a threedimensional morphology. The presence of different functional groups at their outer shell enables them to react with other molecules [1, 2]. The properties of dendrimers can be modified by changing the type and the distribution of the functional groups [3-5]. As a result of unique chemical structures, dendrimers have many interesting properties and applications which have inspired the researchers all over the world. Their applications are in power/energy sectors, engineering, electronics/optoelectronics, and health to name a few [6, 7].

There are two defined methods of dendrimer synthesis: (a) divergent method in which the dendrimer is assembled from a multifunctional core and is extended outward by a series of reactions (Scheme 1), and (b) convergent method in which small units are reacted inward and are attached to a core. Each of these methods has its own pros and cons which can be read elsewhere [8, 9].

Dendrimers are molecules with a tendency to adopt spherical or globular shapes in a solution [10-12]. Other small molecules, depending on their size and charge, can be adsorbed at the outer shell or entrapped within the porous inner shell [13]. A large number of dendrimers with various chemical structures have been synthesized and investigated for adsorption and extraction of organic dyes from aqueous solutions and organic solvents, as illustrated here via an incomplete and arbitrary listing: Poly(propyleneimine) dendrimers for extraction of anionic xanthene dyes from water into organic solvents [14]; Fluorinated dendrimers to extract methyl orange from water into super critical CO₂; Dendritic peptides with carboxylic acid functional groups at the outer surface for extraction of polybasic aromatic dyes from the solution; dendrimers for solubilization of proflavine hydrochloride dye in CH₂Cl₂ [13, 15]. Dendrimers can also be used as capsules that reversibly trap and release guest molecules (e.g. dyes, drugs) [12-16].

Most gemini surfactants are composed of two conventional single chain surfactant molecules chemically bonded together by a spacer. The synthesis and examination of a large number of gemini surfactants with various chemical structures (e.g. anionic, cationic, nonionic, ...) have drawn international attention since 1991 [17-20]. Compared to their monomeric counterparts, gemini surfactants typically have higher surface activity and lower CMC values. Therefore, lesser amount of gemini surfactants is needed for the same applications (e.g. detergency, adsorption, surface modification, etc.) which is very important from economic and environmental points of view [21-23]. Gemini surfactants have been proved to be much more effective than their monomeric counterparts in many different applications [17, 24-26].

Cationic dyes can not migrate freely after being adsorbed on polyacrylonitrile (PAN) fibers. This is due to strong dye-fiber bonding via electrostatic interaction over small temperature range above the glass transition (Tg) of the fiber [27]. The quick rate of dyeing can increase the risk of unlevel dyeing (i.e. non-uniform distribution of dye molecules during adsorption process). This can be prevented by adding retarders (i.e. typically cationic, anionic or polymeric surfactants) to the solution during the dyeing process. Cationic retarders are usually colorless, water-soluble, quaternary ammonium salts containing long aliphatic chains that compete with dye cations for limited anionic sites at the surface of the fiber [27-29]. They reduce the rate of dyeing by lowering the dye concentration gradient across the fiber and enhance dye migration by increasing the total number of cations in the dye-fiber system. There are a few studies on the retarding efficiencies of cationic gemini surfactants [17, 24, 30], but we could not find any similar studies for dendrimers. This research project concerns investigations of the retarding effectiveness of two different generations of poly(amidoamine) (PAMAM) dendrimers (Scheme 1) and two cationic gemini surfactants (Scheme 2) in acrylic dyeing with a cationic dye. Effects of different parameters (i.e. temperature and retarder

concentration) on the kinetic of dyeing process are studied in acrylic dyeing. Moreover, the activation energy of diffusion of the dye into the fiber is investigated.

2. Experimental

2.1. Materials and apparatus

N,*N*-dimethyldodecylamine, 1,3-dibromopropane, 2-dimethylaminoethanol, decanoyl chloride, acetone, ethanol, diethyl ether, magnesium sulfate, and sodium hydrogen carbonate were all purchased from Aldrich for synthesis of the cationic gemini surfactants. For preparation of PAMAM dendrimers, Ethylenediamine, methyl acrylate, and methanol were obtained from Merck Co. All the chemicals and solvents were of analytical reagent grade and used without further purification.

High bulk acrylic yarn 24/2 Nm type , obtained from Nakh Iran Textile Co., was used after washing ,with a nonionic detergent at 40°C for 30 min, and drying processes. A commercial cationic dye, C.I. Basic Red 46 (BR46), was purchased from Dystar Co. and used without further purification. The chemical structure of BR46 is shown in Figure 1. Absorbance changes of dye solutions were measured with a Cecil 9200 double beam UV-Vis spectrophotometer.

Figure 1

2.2. Synthesis of dendrimers and surfactants

Details of synthesis and purification of poly(amidoamine) dendrimers (scheme 1) and cationic gemini surfactants (scheme 2) have been provided in our previous papers [31, 32]. Only a brief description of the synthesis methods is provided here.

2.2.1. Preparation of PAMAM (G=-0.5) and (G=0.5)

PAMAM dendrimers were prepared by the divergent method starting from ethylene diamine as can be seen in Scheme 1. Briefly, a solution of etheylenamine (EA) in methanol was added to methyl acrylate (four molar excess). The mixture was stirred for 5 days at 40 °C. Then, the mixture was evaporated to give PAMAM (G=-0.5) [31, 32].

The solution of PAMAM (G=-0.5) in methanol was added to EA (four molar excess), and the mixture was stirred at room temperature for 3 days. After evaporation of the solvent, the residue was dried completely in 40 $^{\circ}$ C under vacuum to remove the excess amount of EA, and PAMAM (G=0) was obtained. For synthesis of PAMAM (G=0.5), PAMAM (G=0) was reacted with methyl acrylate as it was described elsewhere [31, 32].

Scheme 1

2.2.2. Preparation of cationic gemini surfactants

The procedure for synthesis and purification of the gemini cationic surfactants in this study has been reported in the previous papers in details [17, 23, 24]. The gemini surfactants were synthesized by reacting the tertiary amine with the appropriate dihalide (Scheme 2).

The non-ester-containing cationic gemini surfactant, dodecyl-[3-[dodecyl(dimethyl)ammonio]propyl]-dimethyl-ammonium dibromide (12Q-3-Q12), was synthesized in one step: 1,3-Dibromopropane was added drop-wise to the stirring mixture of *N*,*N*-dimethyldodecylamine (5% excess) in dry acetone and refluxed for 48 h. Upon cooling, a white solid precipitated which was filtered and washed with cold acetone. The product was recrystallized once again and its purity was secured by H NMR analysis.

The ester-containing surfactant, N,N'-bis(2-(dodecanoyloxy)ethyl)-N,N,N',N'-tetramethyl-1,3-propanediammonium dibromide (11E2Q-3-Q2E11), was synthesized in two steps: First, N-(2-(dodecanoyloxy)ethyl)-N,N-dimethylamine was obtained from the reaction of Dimethylethanolamine with dodecyl chloride in dichloromethane ; Second, 11E2Q-3-Q2E11 was synthesized with the reaction of N-(2-(dodecanoyloxy)ethyl)-N,N-dimethylamine with 1,3-Dibromepropane similar to what it was described for 12Q-3-Q12.

Scheme 2

2.3. Acrylic dyeing

Common acrylic fibers dye-able by cationic dyes normally show a finite saturation value associated with the number of available dye-sites at the fiber surface. The most convenient practical definition of fiber saturation is the amount of a cationic dye which after dyeing under conventional condition is found to give 90% exhaustion on to the fiber. The saturation concentration (C_s) of BR46 - acrylic fiber system was obtained to be 5 % over weight of fiber (o.w.f.) based on the standard test procedure [33]. One quarter of the saturation concentration (i.e. 1.25 % o.w.f.) was then chosen to be the initial dye concentration in dye-bath for acrylic dveing for the rest of the experiments. Therefore, the dye concentration is always lower than the amount needed to interact with all the available oppositely charged dye-sites on the fiber.. Dye-baths' pH 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. Acrylic dyeing was investigated at three different temperatures (i.e. 90, 95 and 100 °C), and at various surfactant to dye molar ratios. Dyeing procedure was carried out using a sample dyeing machine (Smart dyer rapid sd-16, India). Absorbance changes of all samples (1 g each) were monitored and determined at certain time intervals (i.e. 5, 10, 15, 20, 30, 60, 90 and 120 min) during the adsorption process. Each dyeing capsule was removed

from the dyeing machine and was cooled down immediately by cold tap water. This procedure was followed by the sample removal from each capsule to quick quenching of the dyeing procedure; The rate of dye adsorption on acrylic fiber drops to a large extent at temperature below the glass transition temperature (T_g) of the fiber (around 85 °C). The percentage of dye adsorption onto acrylic sample or dyebath exhaustion (*E*%) was calculated using Eq. 1:

$$E \% = \frac{(C_0 - C_t)}{C_0} \times 100$$
 Eq. 1

Where, C_0 and C_t are the dye concentrations in the dye-bath solution before and after the dyeing process, respectively.

There was no change in the visible spectra of cationic dye solution in the presence of dendrimers / cationic surfactants. This showed that that there is not apparent interaction between the cationic dye and the cationic dendrimers/surfactants in the solution.

The color strength expressed as K/S was measured according to a previously reported method [29, 32] by the light reflectance technique, and the relative color strength was calculated by applying the Kubetka-Munk equation:

$$K/S = \frac{(1-R)^2}{2R}$$
 Eq. 2

Where, R is the reflectance value of the fabric at peak wavelength, K is the absorption coefficient and S is the scattering coefficient.

Gretag Macbeth (USA) 7000A spectrophotometer under D65 illuminant and 10° observer was used for measuring the colorimetric properties (λ_{max} , L*, a*, b*, C*, h°) and the light reflectance of dyed samples. L* defines lightness; a* denotes the red/green value; and b* the yellow/blue value and C* is the saturation which were calculated from the reflectance data [34-36].The average (Eq. 3) and standard deviation (Eq. 4) of *K/S* values measured at 8

different points on the surface of the dyed samples were used for leveling assessment of dyeing process:

$$(\overline{K/S})_{\lambda} = \frac{1}{n} \sum_{i=1}^{n} (\frac{K}{S})_{i,\lambda}$$
Eq. 3
$$S_{(\lambda)} = \sqrt{\frac{\sum_{i=1}^{n} [(K/S)_{i,\lambda} - (\overline{K/S})_{\lambda}]^{2}}{n-1}}$$
Eq. 4

Where, $S_{(\lambda)}$ is the standard deviation of the *K/S* values and sample mean on each sample point of a dyed fabric; λ is the wavelength of the measurement; n is the total number of the measurements; $(K/S)_{i,\lambda}$ is the *K/S* value of i measurement at λ wavelength. Smaller $S_{(\lambda)}$ can be considered as higher dyeing uniformity [37].

2.4. Empirical kinetic models

Four empirical kinetic models (i.e. parabolic, first order, Cegarra-Puente, and modified Cegarra-Puente) were used for calculation of the dyeing rate constant (*k*) from experimental dye adsorption data at various time intervals of the dyeing process (Equations 5-8) [30, 38]. In all these equations (Eqs. 5-8), C_t is the dye concentration of the sample at time t, C_{∞} is the dye concentration at the equilibrium, *k* is the absorption rate constant and t is the dyeing time.

$$\frac{dC_{t}}{dt} = \frac{k}{C_{t}} \rightarrow C_{t} = k\sqrt{t}$$
Parabolic
Eq. 5
$$\frac{dC_{t}}{dt} = k(C_{\infty} - C_{t}) \rightarrow \ln(1 - \frac{C_{t}}{C_{\infty}}) = -kt$$
Exponential / First Order
Eq. 6
$$\ln(1 - \frac{C_{t}^{2}}{C_{\infty}^{2}}) = -kt$$
Cegarra-Puente
Eq. 7
$$\ln\left[-\ln(1 - \frac{C_{t}^{2}}{C_{\infty}^{2}})\right] = a \times \ln k + a \times \ln t$$
Modified Cegarra-Puente
Eq. 8

2.5. Activation Energy

The apparent activation energy of the diffusion (E_a), the energy that must be overcome in order for a dyeing process to occur, was calculated by the empirical Arrhenius equation Eq. 9 [36]:

$$\ln k = \ln k_0 - \frac{E_a}{RT}$$
 Eq. 9

Where, R is the gas constant (8.314 J/mol K), *k* is the rate constant; and T is the absolute temperature (°K), and E_a is the apparent activation energy of adsorption (J/mol). Plotting the rate of the adsorption against the reciprocal temperature gives a reasonably straight line, the gradient of which is $-E_a/R$ [30, 39].

3. Results and discussion

3.1. Retarding action of dendrimers and surfactants

3.2.1. Effect of temperature

The effect of temperature on the dye absorption (%) at the same molar concentration of retarder to dye was studied. Figure 2 shows that the adsorption of BR46 on acrylic fiber in the absence of retarder is quite fast even at temperature as low as 90 °C. The complete cationic dye adsorption onto the acrylic fiber (i.e. exhaustion in textile terminology) occurs in about 10-20 min. Such a high adsorption rate in dyeing process can result in unlevel dyeing. The presence of dendrimers and cationic surfactants as retarders reduces the dyeing rate and the time needed for the complete dye exhaustion.

Figure 2

As can be seen from Figure 2, the stable gemini cationic surfactant (i.e. 12Q-3-Q12) is the strongest retarder tested and it causes blocking effect (i.e. complete dye exhaustion is not

achievable). Compared with 12Q-3-Q12, the ester-containing cationic gemini surfactant shows somewhat weaker retarding effect as can be seen in Figure 2. This has been discussed in details in our recent publication on retarding efficiencies of ester-containing cationic gemini surfactants [30] and we are not going to repeat the discussion here.

The retarding action of PAMAM dendrimers is weaker than the cationic gemini surfactants. PAMAM (G=-0.5) and PAMAM (G=0.5) have 2 and 6 tertiary amines in their chemical structures, respectively. These groups are quaternized in acidic media by adsorbing protons from the solution (i.e. dyeing pH 4.5). The charge of PAMAM is pH-dependent, and the interactions between PAMAM and the acrylic fiber anionic sites are stronger in acidic pH as the number of cationic groups at PAMAM surface increases. The ester bonds in the chemical structures should be stable in mild acidic condition and the chance of chemical hydrolysis of these groups at mild acidic pH is very low [40]. It should be noted that methyl-ester terminated dendrimers can be hydrolyzed with stoichiometric amounts of NaOH in water to obtain external carboxylate groups with sodium which is not the case here [41].

Lower retarding action of these cationic PAMAM dendrimers (at pH 4.5) compared with those of cationic gemini surfactants suggests that the charge density of the dendrimers is lower than that of the geminis. So, the cationic dendrimers with larger molecular size and lower charge density are weaker retarders.

The retarding action of PAMAM (G=-0.5) is weaker than that of PAMAM (G=+0.5).

PAMAM (G=0.5), with larger molecular size and having 6 cationic groups in its structure, adsorb on the anionic sites of acrylic fiber somewhat better than PAMAM (G=-0.5) with smaller molecular size and having 2 cationic groups.

The segmental motion of polymer molecules increases with temperature increase above the Tg of acrylic fiber. Therefore, additional cationic dye molecules can diffuse and find new anionic dye-sites at and within the fiber (i.e. the dye adsorption rate increases). Fast dyeing

process is the main reason behind the dyeing unlevelness and non-uniform adsorption of cationic dye molecules at the surface of the acrylic fiber. Considering the thermoplasticity of acrylic fibers, it would not be advisable to prolong the dyeing process at high temperatures in order to improve the dyeing levelness. The dye adsorption rate should be controlled from the beginning of the dyeing process [42-44].

3.1.2. Effect of retarder concentration

The effect of retarder concentration on the cationic dye adsorption onto acrylic sample at initial dye concentration of 1.25 % (o.w.f) was investigated at 100 °C for the dendrimers and the cationic gemini surfactants (Figure 3). The results clearly showed that: (a) in the absence of any retarder, the dye adsorption onto acrylic fiber is very fast (i.e. 100% dye adsorption in less than 15 min), (b) the rate of dye adsorption decreases in the presence of the dendrimers and the surfactants, (c) the rate of dye adsorption decreases by increasing the retarders' concentration.

The retarding effect of the investigated retarders is as follows: 12Q-3-Q12 > 11E2Q-3-Q2E11>= PAMAM (G=0.5) > PAMAM (G=-0.5). It seems the charge density of the retarders plays an important role on their retarding action. Both of the dendrimers have cationaizable groups (i.e. tertiary amine) in their structures. These groups can be quaternized in acidic media by adsorbing proton from aqueous solution. Therefore, they have weaker charge density than the cationic gemini surfactants with permanent cationic head groups.

As can be seen from the Figure 3, the stable gemini surfactant (i.e. 12Q-3-Q12) has shown a blocking effect (i.e. 100% dye absorption has not been reached even after 120 min). 11E2Q-3-Q2E11 and the dendrimers have not shown such a problem (i.e. permanent blocking effect) which is beneficial from dyeing point of view. This suggests that inserting an electron withdrawing group (e.g. ester bond or amide) in the chemical structure of a cationic retarder

in a close distance from the cationic group can reduce the charge density of the retarder and decrease the oppositely charged interactions between the cationic retarders and the anionic sites of acrylic fiber which solves the blocking effect of the cationic retarders.

Figure 3

3.2. Leveling Properties Analysis

The colorimetric properties of dyed acrylic fibers and K/S values were measured by reflection spectrophotometer (Table 1). The colorimetric data confirmed that the dyed samples in the presence of retarders had a difference as compared with the sample of no retarder. In general, dyed fibers in the presence of retarders were light and bright. The results from Table 1 clearly indicate that the lightness (L*) of dyed fibers in the presence of retarders follow the order: 12Q-3-Q12 > 11E2Q-3-Q2E11 > PAMAM G=0.5 >= PAMAM G=-0.5. In addition, *K/S* values of the dyed samples were noticeably lower for the cationic gemini surfactants in comparison to those of the dendrimers showing that surfactants are much stronger retarders than the dendrimers.

The leveling properties in acrylic dyeing (i.e. uniform dye adsorption) in the presence of the retarders are given in Table 1. The results indicated that the difference of the $S_{(\lambda)}$ is distinct, and the retarding agents are basically able to meet the actual production applications for its uniform dyeing performance [37].

Retarding agent	L*	a*	b*	c*	h	$\overline{K/S}$	$\mathbf{S}_{(\lambda)}$
No retarder	38.53	59.37	11.05	60.38	10.54	33.84	1.09
PAMAM, G=-0.5	41.46	62.99	12.29	64.17	11.04	27.28	0.97
PAMAM, G=0.5	43.47	62.49	11.77	63.59	10.67	25.68	0.95
11E2Q-3-Q2E11	46.81	57.91	3.70	58.03	3.65	14.02	0.93
12Q-3-12Q	51.7	56.55	2.06	56.59	2.09	7.94	0.87

Table 1. Results of various leveling properties of BR46 on acrylic fibers in λ_{max} =530 at dye: retarding agent molar ratio: 0.5, time 30 min, and temperature 100 °C

3.2. Kinetic study

The empirical kinetic models (Equations 5-8) were employed to obtain the dyeing rate constant (*k*). The *k* values along with the correlation coefficients (\mathbb{R}^2) for various dyeing systems in the absence and presence of various concentrations of retarders are reported in Table 2. Twenty three different dyeing systems were studied by these models, and based on the obtained regression coefficients, the modified Cegarra-Puente empirical model (Eq. 8) showed somewhat better fit with the dyeing kinetics (i.e. the average and minimum of \mathbb{R}^2 values were 0.99 and 0.975. respectively). The values obtained from the Cegarra-Puente empirical model (Eq. 7) have not been reported in this table as the correlation was even poorer than that of the exponential model (Eq. 6).

Table 2. Dyeing rate constants and regression coefficients based on three different empirical kinetic models for dyeing the acrylic fiber with BR46 in the absence and presence of the retarders

		Para	ıbolic	First (Order	Modifie	d Cegarra-
Retarding agent	C (molar	(Eq. 5)		(Eq. 6)		Puente (Eq. 8)	
	Tatio)	k	\mathbf{R}^2	k	\mathbf{R}^2	k	\mathbf{R}^2
No-retarder	-	0.280	0.926	0.272	0.951	0.244	0.991
	0.25	0.137	0.915	0.135	0.984	0.116	0.988
PAMAM, G=-0.5	0.5	0.094	0.859	0.088	0.967	0.090	0.985
	0.75	0.087	0.889	0.076	0.955	0.081	0.979
	0.25	0.085	0.956	0.027	0.970	0.094	0.990
PAMAM, G=0.5	0.5	0.081	0.961	0.022	0.803	0.079	0.975
	0.75	0.076	0.958	0.018	0.878	0.070	0.986
	0.25	0.031	0.919	0.011	0.886	0.011	0.995
12Q-3-12Q	0.5	0.055	0.962	0.012	0.910	0.009	0.988
	0.75	0.044	0.988	0.008	0.964	0.003	0.992
	0.25	0.073	0.945	0.064	0.903	0.015	0.993
11E2Q-3-Q2E11	0.5	0.026	0.983	0.013	0.958	0.010	0.981
	0.75	0.055	0.974	0.027	0.962	0.007	0.978
\mathbf{R}^2 min)		0.859		0.803		0.975
R ² average			0.941		0.930		0.986

The *k* values in the presence of various retarders are as follows: 12Q-3-Q12 < 11E2Q-3-Q2E11 < PAMAM G=0.5 < PAMAM G=-0.5 < no retarder. In addition, the*k*values were noticeably lower for the cationic gemini surfactants in comparison to those of the dendrimers

showing that surfactants are much stronger retarders than the dendrimers. The results illustrate that in lower concentrations of retarders, k values are more than when the retarders exist at higher concentrations. Moreover, the k values in the presence of various retarders follow the order: 12Q-3-Q12 < 11E2Q-3-Q2E11 < PAMAM G=0.5 < PAMAM G=-0.5 < no retarder. In addition, <math>k values were noticeably lower for the cationic gemini surfactants in comparison to those of the dendrimers showing that surfactants are much stronger retarders than the dendrimers.

Absorption rate constants at different temperatures are also given in Table 3. 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. In the systems studied, the correlation coefficients of the model were higher than those of other models. The results indicated that when the temperature is increased, the k values are enhanced. As we can see from Table 3, the k values of dendrimers are lower than that of surfactants.

Table 3. The constant rate and correlation coefficients in the acrylic dyeing with cationic

 dyes in the presence of dendrimers and surfactants at different temperatures

	Т	Parabolic		First Order		Modified Cegarra-	
Retarding agent	°(C)	(Eq. 5)		(Eq. 6)		Puente (Eq. 8)	
		k	\mathbf{R}^2	k	\mathbf{R}^2	k	R ²
	90	0.146	0.937	0.133	0.955	0.118	0.989
No-retarder	95	0.218	0.949	0.204	0.968	0.155	0.975
	100	0.280	0.926	0.272	0.951	0.244	0.991
	90	0.104	0.969	0.033	0.924	0.027	0.996
PAMAM, G=-0.5	95	0.112	0.829	0.042	0.890	0.048	0.993
	100	0.094	0.919	0.088	0.905	0.090	0.996
	90	0.128	0.935	0.046	0.896	0.020	0.990
PAMAM, G=0.5	95	0.123	0.896	0.059	0.847	0.032	0.981
	100	0.121	0.961	0.037	0.803	0.079	0.975
	90	0.035	0.969	0.004	0.924	0.001	0.996
12Q-3-12Q	95	0.055	0.962	0.012	0.910	0.006	0.988
	100	0.031	0.919	0.011	0.886	0.011	0.995
_	90	0.026	0.984	0.003	0.954	0.005	0.993
11E2Q-3-Q2E11	95	0.067	0.979	0.023	0.936	0.011	0.998
	100	0.073	0.945	0.264	0.903	0.015	0.993
R ² min			0.829		0.803		0.975
R ² average			0.938		0.898		0.991

The rate constants obtained from the modified Cegarra-Puente model are depicted vs. temperature for the dendrimers and cationic gemini surfactants (Figure 4). In the absence of any retarder, there is a big difference between the apparent rate constants of acrylic dyeing as

it can be seen from the Figure 4. The values of dyeing rate constants are in the order of: 12Q-3-Q12<11E2Q-3-Q2E11<PAMAM G=0.5<PAMAM G=-0.5. As we have already discussed, 12Q-3-Q12 is the strongest retarder among all other investigated retarders.

Figure 4

3.3. Activation energy

The apparent activation energy of dyeing is defined as the amount of energy required for dye molecules to overcome the resistance of the adsorbate matrix to diffuse. A lower value of E_a means faster diffusion of dye molecules into the cross-sectional matrix and a lower dependence on the temperature. The apparent activation energies were determined from the absorption rate constants at different temperatures using the Arrhenius equation (Eq. 8). One may obtain the activation energy from the slope of ln k curve versus 1/T, and the correlation coefficients of the fit are also obtained (Table 4). A significant increase in the activation energy can be observed when the retarders are used. 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 as follows: no retarder<PAMAM G=-0.5< PAMAM G=0.5< 11E2Q-3-Q2E11<12Q-3-Q12 and this could be attributed to the charge density of cationic retarder as we discussed earlier.

Table 4. The activation energy in acrylic dyeing process with cationic dyes in the presence of dendrimers and surfactants

Retarding agent	Ea(kJ/mol)	\mathbf{R}^2
No retarder	122.86	0.998
PAMAM, G=-0.5	135.49	0.998
PAMAM, G=0.5	144.97	0.964
11E2Q-3-Q2E11	175.50	0.935
12Q-3-12Q	223.33	0.966

4. Conclusion

The conclusion remarks of this research work are as follows:

- The order of retarding and blocking strength of the retarders in the dyeing process was as follows: 12Q-3-Q12 > 11E2Q-3-Q2E11 > PAMAM G=0.5> PAMAM G=-0.5.
- The dendrimers are protonated at acidic pH 4.5 and act as cationic retarders in the same way as cationic surfactants do
- Two cationic gemini surfactants were much stronger retarders possibly because of their higher charge density per each molecule.
- The rate of dyeing process increased with temperature increase.
- The rate of dyeing process decreased by increasing the retarders' concentration.
- The modified Cegarra-Puente model fitted the dyeing kinetic data somewhat better than the other empirical kinetic models
- The presence of an electron withdrawing group (e.g. ester bond or amide) in the chemical structure of a cationic retarder in the close distance from the cationic group can reduce the charge density of the retarder and decrease the oppositely charged interactions between the cationic head groups of the retarders and the anionic dyesites of the acrylic fiber.

References

[1] Vogtle F, Richard G, Werner N. Dendrimer Chemistry. Wiley-VCH, Weinheim, 2009.

[2] Froehling PE. Dendrimers and dyes - a review. Dyes Pigments 2001; 48: 187-195.

[3] Chen CZ, Beck-Tan NC, Dhurjati P, VanDyk TK, LaRossa RA, Cooper SL. Quaternary ammonium functionalized poly(propylene imine) dendrimers as effective antimicrobials: structure-activity studies. Biomacromolecules 2000; 1: 473-480.

[4] Burkinshaw SM, Froehling PE, Mignanelli M. The effect of hyperbranched polymers on the dyeing of polypropylene fibres. Dyes Pigments 2002; 53: 229-235.

[5] Suek NW, Lamm MH. Effect of Terminal Group Modification on the Solution Properties of Dendrimers: A Molecular Dynamics Simulation Study. Macromolecules 2006; 39: 4247-4255.

[6] Hay G, Mackay ME, Hawker CJ. Thermodynamic Properties of Dendrimers Compared with Linear Polymers: General Observations. Journal of Polymer Science: Part B: Polymer Physics 2001; 39: 1766-1777.

[7] Klajnet B, Bryszewska M. Dendrimers: properties and application. Acta Biochemica Polonica 2001; 48: 199-208.

[8] Astruc D, Boisselier E, Ornelas C. Dendrimers Designed for Functions: From Physical, Photophysical, and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular. Chem. Rev. 2010; 110: 1857-1959.

[9] Sperling LH. Introduction to Physical Polymer Science. John Wiley & Sons, Inc., 2006.

[10] Sadeghi-Kiakhani M, Arami M, Gharanjig K. Dye removal from colored textile wastewater using chitosan-PPI dendrimer hybrid as a biopolymer: optimization, kinetic and isotherm studies. J Appl Polym Sci 2013; 127: 2607-2619.

[11] Newkome GR, Shreiner CD. Poly(amidoamine), polypropylenimine, and related dendrimers and dendrons possessing different 1/2 branching motifs: An overview of the divergent procedures. Polymer 2008; 49: 1-173.

[12] Tomalia DA, Frechet J M. Discovery of dendrimers and dendritic polymers: a brief historical perspective. J. Polym. Sci. Part A Polym. Chem. 2002; 40: 2719-2728.

[13] Smith DK, Supramolecular dendritic solubilisation of a hydrophilic dye and tuning of its optical properties. Chem. Commun. 1999, 1685-1686.

[14] Cooper AI, Londono JD, Wignall G, McClain JB, Samulski ET, Lin JS, Dobrynin A,Rubinstein M, Burke AL C, Fréchet JMJ, DeSimone JM, Nature 1998; 389: 368.

[15] Smith DK, Diederich F., Functional Dendrimers: Unique Biological Mimics, Chemistry-A European Journal, 1998; 4: 1353-1361.

[16] Liljefors T, Norrby PO. An *ab* Initio Study of the Trimethylamine-Formic Acid and the Trimethylammonium Ion<u>-</u>Formate Anion Complexes, Their Monohydrates, and Continuum Solvation J Am Chem Soc 1997; 119: 1052-1058.

[17] Tehrani-Bagha AR, Bahrami H, Movassagh B, Arami M, Amirshahi SH, Menger FM.Dynamic adsorption of gemini and conventional cationic surfactants onto polyacrylonitrile,Colloids Surfaces A 2007; 307: 121-127.

[18] Menger FM, Keiper JS. Gemini Surfactants, Angew Chem Int Ed. 2000; 39: 1906-20.

[19] Zana R, Xia J. Gemini Surfactants. New York: Marcel Dekker, 2004.

[20] Zeydan M, Yazıcı D. Improvement of process conditions in acrylic fiber dyeing using gray-based Taguchi-neural network approach, Neural Computing and Applications 2014; 25: 155-170.

[21] Zana R, Benrraou M, Rueff R, Alkanediyl- α , ω -bis(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree, Langmuir. 1991; 7: 1072-1075.

[22] Mahdavian M, Tehrani-Bagha AR, Holmberg K. Comparison of a cationic gemini surfactant and the corresponding monomeric surfactant for corrosion protection of mild steel in hydrochloric acid, J Surfactants Deterg. 2011; 14: 605-613.

[23] Tehrani-Bagha AR, Kärnbratt J, Löfroth JE, Holmberg K. Cationic Ester-containing Gemini Surfactants: Determination of Aggregation Numbers by Time-Resolved fluorescence quenching, J Colloid Interf Sci. 2012; 376: 126-32.

[24] Tehrani-Bagha AR, Holmberg K. Cationic Ester-Containing Gemini Surfactants: Physical-Chemical Properties, Langmuir. 2010; 26, 9276-82.

[25] Motamedi M, Tehrani-Bagha AR, Mahdavian M. A comparative study on the electrochemical behavior of mild steel in sulfamic acid solution in the presence of monomeric and gemini surfactants, Electrochimica Acta. 2011; 58, 488-96.

[26] Mahdavian M, Tehrani-Bagha AR, Holmberg K. Comparison of a cationic gemini surfactant and the corresponding monomeric surfactant for corrosion protection of mild steel in hydrochloric acid, J Surfactants Deterg. 2011;14: 605-13.

[27] Beckmann W, Nunn DM. The Dyeing of Synthetic-Polymer and Acetate Fibres, Dyers Company, 1979.

[28] David R., Geoffrey H. The Chemistry and Application of Dyes, New York and London, 1990.

[29] Broadbent AD. Basic Principles of Textile Coloration, The Society of Dyers and Colourist, Bradford, 2001.

[30] Sadeghi-Kiakhani M., Tehrani-Bagha AR, Cationic ester-containing gemini surfactants as retarders in acrylic dyeing. Colloids and Surfaces A: Physicochem. Eng. Aspects 2015; 479: 52-59.

[31] Esfand R, Tomalia DA. Laboratory synthesis of poly(amido amine) dendrimers. In:Frechet, J.M.J., Tomalia, D.A. (Eds.), Dendrimers and Other Dendritic Polymers. John Wiley& Sons Ltd., Baffins Lane, Chichester, 2002: 587-604.

[32] Sadeghi-Kiakhani M, Safapour S. Improvement of the dyeing and fastness properties of a naphthalimide fluorescent dye using poly(amidoamine) dendrimer. Color. Technol., 2015; 131: 142-148.

[33] Beckmann W, Determination of the Saturation Characteristics of Basic Dyes and AcrylicFibres, JSDC 1973, 89: 292-295.

[34] Sadeghi-Kiakhani M, Gharanjig K, Arami M, Khosravi A. Dyeing and Fastness Properties of Polyamide Fabrics Using Some Acid-Based Monoazo Disperse Dyes. Journal of Applied Polymer Science 2011, 122: 3390-3395.

[35] Wyszecki G, Stiles WS. Color science concepts and methods, quantitative data and formulae. Wiley, New York, 2000.

[36] Ford A, Roberts A Colour space conversions. Westminster University, London, 1998.

[37] Zhang Z, Yuan A, Wang H, Zhu L, Xu H, Zheng C. Effects of solvent properties on cationic dyeing process of acrylic yarn. Korean J Chem Eng 2014; 31(4): 719-723.

[38] Cegarra J, Puente P, Fiadeiro JM. Kinetics of Dyeing Acrylic Fibres with Cationic Dyes in the Presence of Polyethoxylated Amines, JSDC 1986; 102: 274.

[39] Kanth SV, Venba R, Jayakumar GC, Chandrababu NK. Kinetics of leather dyeing pretreated with enzymes: Role of acid protease. Bioresource Technology 2009; 100: 2430-2435.

[40] Tehrani-Bagha AR, Holmberg K, van Ginkel CG, Kean M. Cationic gemini surfactants with cleavable spacer: Chemical hydrolysis, biodegradation, and toxicity, J. Colloid Interface Sci. 2015, 449, 72-79.

[41] Esumi K, Goino M. Adsorption of Poly(amidoamine) Dendrimers on Alumina /Water and Silica/Water Interfaces. Langmuir 1998, 14: 4466-4470

[42] Yu C, Chen Y. Study on Dyeing Properties of Functional Acrylic Fiber, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry 2006; 43: 1695-1702.

[43] Bird CL, Boston WS. The Theory of Coloration of Textiles. London: Dyers Company Publications Trust; 1975.

[44] Burkinshaw SM. Chemical Principles of Synthetic Fibre Dyeing, Blackie Academi & Professional, Chapman & Hall, 1995.

Figure captions:

Figure 1. Chemical structure and Physical-Chemical Properties of Basic Red 46 (BR46)

Scheme 1. Preparation of PAMAM dendrimers

Scheme 2. Syntheses of two cationic gemini surfactants: (a) 12Q-3-Q12, and (b) 11E2Q-3-

Q2E11.

Figure 2. Dye absorption (%) of dyes onto acrylic fiber in the presence of retarders (molar ratio to dye=0.5) at different temperatures.

Figure 3. Dye absorption (%) of BR46 onto acrylic fiber in the absence and presence of the

dendrimer (G=-0.5) and GS (molar ratios to dye= a) 0.25 and b) 0.75 at 100 °C.

Figure 4. Variation of the dyeing rate constants by temperature in the absence and presence of

the retarders



Molecular Weight: 401g/mol;

Molecular Formula:C₁₈H₂₁BrN₆;

Solubility in water (30 °C): 80 g/L;

 λ_{max} =530 nm

Figure 1





2 3 4 5 6 7 8 9 10 11 12 13 14 15 $\begin{array}{c} 16\\ 17\\ 18\\ 20\\ 222\\ 23\\ 24\\ 25\\ 27\\ 28\\ 20\\ 312\\ 33\\ 35\\ 36\\ 37\\ 39\\ 40\\ 42\\ 44\\ 45\\ 46\\ \end{array}$ 51 52 53









ьз





Highlights

- The effect of PAMAM dendrimers was studied on the dyeability of acrylic fibers.
- The dye adsorption kinetic at various conditions was investigated.
- The empirical modified Cegarra-Puente model fitted the dyeing kinetic data
- The activation energy of diffusion of the dye into the fiber was calculated.