

# Dyeing cotton in alkane solvent using polyethylene glycol-based reverse micelle as reactive dye carrier

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**Abstract** The dyeability of cotton fabrics with reactive dye, in non-aqueous alkane medium of heptane and octane was investigated using a non-ionic surfactant reverse-micellar approach comprising of poly(ethylene glycol)-based surfactant. The reactive dye was satisfactorily encapsulated in the cavity of the reverse micelle under the optimised process parameters as measured by the colour yield. Dyeability of cotton fibre with reactive dye from the reverse micellar solution was improved even in the absence of electrolytes. Optimisation of dyeing and fixation process could be achieved in a one-bath reverse-micelle solution. Experimental results revealed that dyeability in the alkane-assisted dyeing process is better than that in conventional water-based dyeing without incorporation of electrolytes. The scanning electron microscopic images showed no obvious surface damage from heptane or octane but some microfibrils were noticed.

**Keywords** Cotton fibre · Non-ionic surfactant · Non-aqueous dyeing · PEG · Reverse micelle · Reactive dye

## Introduction

Water-based textile dyeing and the subsequent aqueous washing process have undesirable environmental impacts such as discharge of chemical pollutants and large amount of coloured wastewater. In recent decades, new dyeing technologies that avoid the use of water as a solvent have been developed. According to previous reports, it has become obvious that synthetic fibres such as polyester, polyamide, etc. can be dyed satisfactorily with hydrophobic disperse dyes (Saus et al. 1992; Knittel et al. 1993). Other synthetic fibers such as poly(ethylene terephthalate) (PET) can be incorporated with nanoclay particles in order to improve the dyeability (Gashti and Moradian 2012) and one-step dyeing of nylon 6 fabric with disperse-reactive, hydrophobic-reactive and antimicrobial disperse azo dyes using supercritical CO<sub>2</sub> as transport medium. (Liao et al. 2000; Liao 2004; Elmaaty et al. 2015). On the other hand, dyeing of natural fibres such as cotton, wool and silk etc. with conventional hydrophilic reactive dyes in non-aqueous solvent has not been systematically established as yet. The structure of reactive dyes is compatible with cotton fibre structure due to chemical bonding

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between suitable groups in the dye molecule and hydroxyl groups of the cotton fibre. In textile processing, cotton is compatible with aqueous medium in terms of wettability. However, the same hydrophilic nature of water and cotton fibre inevitably compromises the dyeing efficiency because water shares a similar reactive functionality with cotton. Side products generated from competing hydrolysis remain in the processing bath and require extra effluent treatment. In reactive dyeing of cotton fibre, the consumed liquor may contain up to 30 % of the applied dyes in the non-recoverable hydrolysed form (Reife and Freeman 1996) which implies complicated post-treatment of dyeing effluents (Allegre et al. 2006). Conventional reactive dye dyeing and other forms of wet processing of cotton involve substantial amounts of salt electrolytes, which require tedious steps to separate from aqueous medium (Vandevivere et al. 1998; Marcucci et al. 2001; Fersi and Dhahbi 2008). Furthermore, the volume of water consumed in wet processing of cotton may cause significant environmental impacts (Hickman 1993). In textile industry, new methodologies and technologies have been developed in order to improve the dyeability of cotton. It was suggested that the cotton fibre surface pretreated by nano-scale clay mineral particles contributed to higher dyeability with direct and basic dyes. (Gashti et al. 2013). Other modification of cotton fiber surface using 3-(chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC) to cationize cotton surface and effectively improves dye uptake properties of cotton fabric without the addition of salt electrolytes (Hashem et al. 2003; Kanik and Hauser 2004; Montazer et al. 2007; Wang et al. 2009; Patiño et al. 2011; Acharya et al. 2014).

To investigate the possibility of switching the dyeing medium from aqueous to non-aqueous (organic solvents), it needs to be examined whether competing hydrolysis can be eliminated, so that the dyeing bath could be reusable and more environmentally friendly. For similar reasons, non-aqueous reactive dye dyeing of cotton had been attempted employing chlorinated hydrocarbon as solvent (Chavan and Subramanian 1983) and supercritical carbon dioxide (Ikushima et al. 1989). However, poor evenness was the major problem associated with these systems because of insufficient swelling of cotton and highly limited solubility of the reactive dyes. For the supercritical carbon dioxide system, improvement of colour evenness

could be achieved by introducing auxiliaries such as ethanol or methanol to modify the polarity of the dyeing medium (Ikushima et al. 1989). However, no significant improvement in the solubility of water-soluble dyes is observed with this technique.

In textile processing, water-soluble dyes can be well dispersed in non-aqueous solvent with the aid of reverse micelles (Pileni 1989; Barzykin and Tachiya 1994). Reverse micelles are self-assembled aggregates formed by surfactants in organic solvent and water pools of nanoscale are formed by solubilisation of water in their polar or hydrophilic cores (Pileni 1993). The reverse micelles that are mostly with spherical shape are usually formed in ternary surfactant-water-organic solvent mixtures including surfactants (<10 %), water (0–10 %) and organic solvent (80–90 %), so the reverse micelles are also called water-in-oil emulsions. Moreover, reverse micellar systems are colloidal solutions, so characteristic properties of these systems are thermodynamic stability (no phase separation with time), spontaneous formation, low interfacial tension ( $<10^{-2}$  mN m<sup>-1</sup>), transparent nature (nanometer size <100 nm), large surface area (10<sup>2</sup>–10<sup>3</sup> m<sup>2</sup> cm<sup>-3</sup>), viscosity comparable with pure organic solvents and highly dynamic (Reife and Freeman 1996). In general, reverse micelles are formed from a surfactant or surfactant and co-surfactant pair dissolved in a non-aqueous phase. Water and hydrophilic molecules are solubilised inside the reverse micelle which can swell the micelles to many times their empty size (De and Maitra 1995). Reverse micelle has a remarkable property to solubilise a small amount of water at the interior of the micelle and to provide a stable aqueous microenvironment, the so-called water-pool, in non-aqueous media (Fendler 1982).

Sawada et al. (2004) investigated the dyeing of natural fibres in reverse micellar system in supercritical carbon dioxide. However, the strategy for this dyeing method had a problem. Not all kinds of water-soluble dyes were solubilised in the interior of reverse micelles because the size of the self-assembled micellar aggregates was not enough to incorporate bulky dyes. Thus, reverse micelles with appropriate surfactant structure is significant for encapsulation of some water soluble dyes with high molecular weight and good affinity between surfactants and water soluble dyes.

Reverse micelles used in the textile dyeing process are those prepared with anionic surfactant as the building block, especially Aerosol-OT. The extant

literature has reported that an ionic header group in the water-pool may play a role as a dye auxiliary and the dye adsorption on textile fibre is strongly affected by the charge of surfactant molecules (Sawada and Ueda 2003). The ionic functional groups of the surfactant molecules used in reverse micelles have adverse effects on polarity of the confined “water-pool” and the uneven aqueous micro-environment due to electrostatic charge interaction revealed a negative effect on the application of reverse micelles such as controlled release of reactive dye on the textile materials surface and the competitive dye adsorption on both textile surface and ionic groups of the reverse micelles. Nonionic surfactant-based reverse micelle with rigid aromatic hydrocarbon structure such as Triton X-100 was not well dispersed in aliphatic hydrocarbon solvent and did not show obvious positive effect on dyeability based on adsorption kinetic curves and measured K/S values (Yi et al. 2012; Harrison et al. 1994; Johnston et al. 1996). Clarke et al. (1997) synthesised a fluorinated surfactant to assemble a thermodynamically stable reverse micelle but the fluorinated surfactants are not commercially available and cause environmental hazard.

To the best of our knowledge, use of poly(ethylene glycol)-based (PEG-based) nonionic surfactant-based reverse micelles as dye water-pool carrier in solvent-assisted cotton dyeing has not been reported in the literature. Therefore, it would be worth looking into a systematic study of developing a novel cotton dyeing process using nonionic surfactant poly(ethylene glycol) (12) tridecylether ( $C_{13}H_{27}(OCH_2CH_2)_nOH$ ) ( $n \sim 12$ ) to encapsulate reactive dye as reverse micellar structure. The encapsulation property is inherently controlled by two balanced forces: (1) hydrophilic interaction between the hydrophilic poly(ethylene glycol) with repeating unit of ethylene oxide ( $OCH_2CH_2$ ) and the reactive dye; and (2) the interaction between hydrophobic segment (decylether) and the organic solvent. The repeating unit of ethylene oxide (EO) is actually not an extremely hydrophilic group. Moreover, any change in temperature that affects the interaction between the repeating EO chains and the water/oil interfacial environment is likely to affect the behavior of the micellar structure.

In order to boost the effectiveness of dyeability and minimise materials and energy requirements, we developed a one-bath process to achieve both high quality dyeing and colour fixation process system

using alkane-based solvent as dyeing medium. The purpose of the present study is accumulation of fundamental knowledge of dyeing of cotton with reactive dyes in PEG-based reverse-micellar systems. In our study, dyeability and fixation of reactive dyes on cotton in a reverse-micellar system have been determined. In the fixation process, the effect of alkali content on fixing ratio has also been studied. In addition, the possibility of fixation of reactive dyes in this system without the use of salt has also been examined.

## Experimental

### Materials and reagents

Commercially ready-for-dyeing knitted fabric was first cleaned with a solution containing 2 g/L soda ash and 2 g/L soap with a thermal-control shaker at temperature of 90 °C for 30 min. After cleaning, the fabric was thoroughly rinsed with cold water and dried at room temperature. The cleaned fabrics were conditioned at relative humidity of  $65 \pm 2\%$  and  $20 \pm 2\%$  for at least 24 h prior to further experiment. The nonionic surfactant, poly(oxyethylene glycol) (12) tridecylether ( $C_{13}H_{27}(OCH_2CH_2)_nOH$ ) ( $n \sim 12$ ) was of reagent grade. Heptane and octane were used as organic solvent and *n*-octanol was used as co-surfactant in the dyeing process. Both solvent and co-surfactant were of reagent grade. Three reactive dyes (types of Levafix CA Red, Levafix CA Blue and Levafix CA Yellow provided by Dystar, China) were used directly without further purification.

### Cotton dyeing and fixation using water (with salt)

The liquor-to-goods ratio was 50:1. The amount of salt added is based on concentration of reactive dye used (percentage on weight of fibre, % owf) as listed in Table 1. Figure 1 is the dyeing curve of the water-based dyeing. Firstly, the cotton fabric was immersed in the dyeing solution (containing dye and salt) and the dyeing solution was kept at 30 °C with shaking for 10 min. After 10 min, temperature of the dyeing solution was increased to 70 °C at a heating rate of 2 °C/min with 110 shakes per minute. The dyeing was carried out at 70 °C for 40 min. After dyeing, soda ash was added for dye fixation; the amount was based on

**Table 1** The required concentration of salt (NaCl) and soda ash at various weight percentages of reactive dye

Liquor ratio 50:1, 70 °C						
Dye	% on weight of fibre (% owf)	0.5	1.5	2.5	3.5	6
Salt (NaCl)	g/L	20	42.5	55	65	80
Soda ash	g/L	5	5	5	5	5

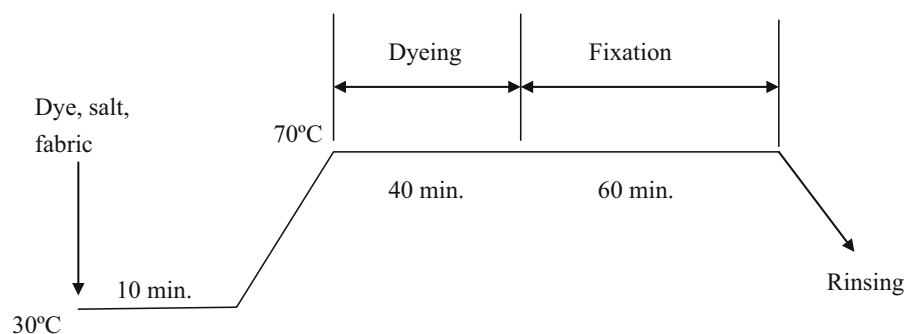
**Fig. 1** The workflow of cotton dyeing and fixation using water (with salt)

Table 1. The dye fixation was conducted at 70 °C (with 110 shakes per minute) for 60 min. After fixation, the cotton fabric was then immersed in soap solution (2 g/L) and rinsed for 15 min at 25 °C. The rinsed cotton fabric was then rinsed with water and was air-dried. The dried and dyed fabrics were then conditioned at relative humidity of  $65 \pm 2\%$  and  $20 \pm 2\%$  for at least 24 h prior to further experiment.

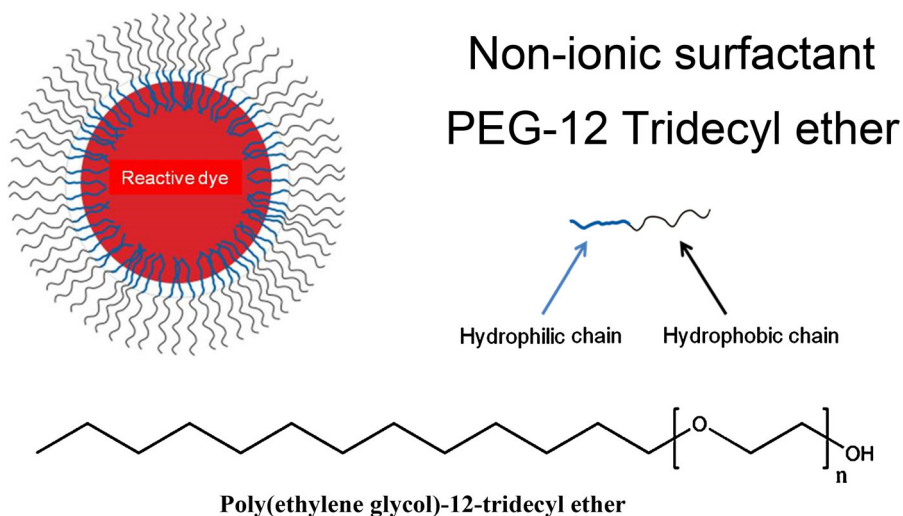
#### Preparation of reverse micelle encapsulated dye

Series of PEG-based reverse micelle was prepared by a simple injection method at room temperature. The non-ionic surfactant and co-surfactant (*n*-octanol) were first premixed (with agitation) to achieve different surfactant to co-surfactant ratios ranging from 0.05:1 to 0.025:1. Then the surfactant/co-surfactant mixture was dissolved in heptane and octane in order to obtain organic surfactant solution for facilitating the self-assembly of PEG-based reverse micelle (Fig. 2). A controlled amount of reactive dye aqueous solution was then applied into the reverse micellar system dropwise. After injection of the dye solution, the mixtures were vigorously stirred for 2 min until the well dispersed solution with reverse micelle encapsulated reactive dye was obtained.

Cotton dyeing and fixation using PEG-based reverse micelle approach in heptane and octane (without salt)

A series of dyeing experiments with PEG-based reverse micelle systems were carried out. Cleaned cotton fabric was immersed in the reverse micelle solution at 30 °C with shaking for 10 min. Then the temperature was increased to different dyeing temperature (40, 50, 60, 65, 70 or 75 °C) and 110 shakes per minute at a rate of 2 °C/min; Different dyeing time (10, 20, 30, 40, 50 or 60) was used. After dyeing, a controlled amount of soda ash aqueous solution was added (Table 2) into the dyeing bath and the fixation was conducted at different temperature (40, 50, 60, 65, 70 or 75 °C) for different time (10, 20, 30, 40, 50 or 60 min). After fixation, the cotton fabric was immersed in soap solution for 15 min at 25 °C. The fabric was then rinsed with water and air-dried. The dried and dyed fabrics were then conditioned at relative humidity of  $65 \pm 2\%$  and  $20 \pm 2\%$  for at least 24 h prior to further experiment. The flow of the whole process is shown in Fig. 3. In order to optimise cotton dyeing and fixation using reverse micelle approach, octane and Levafix Red CA were used as the solvent and the dye, respectively, for optimisation. The optimised dyeing

**Fig. 2** PEG-based reverse micelle encapsulated reactive dye and structure of nonionic surfactant (poly(ethylene glycol)-12-tridecyl ether)



**Table 2** Colour fixation (soda ash) concentration used

Dye concentration (% owf)	Colour fixation agent to cotton weight ratio (g/g)
0.5	0.02
	0.04
	0.06
1.5	0.06
	0.07
	0.08
2.5	0.08
	0.085
	0.09
3.5	0.09
	0.095
	0.10
6	0.115
	0.12
	0.125

and fixation process was applied using heptane. The optimisation parameters included: (1) solvent volume to cotton weight ratio (6:1, 8:1, 10:1 and 15:1); (2) surfactant to co-surfactant mole ratio (1:4, 1:5, 1:6, 1:7 and 1:8); (3) surfactant to water mole ratio (0.05:1, 0.04:1, 0.033:1 and 0.025:1); (4) volume of water-pool for dye (in mL) (0.3, 0.4, 0.5, 0.6 and 0.7); (5) volume of water-pool for soda ash (in mL) (0.3, 0.4, 0.5, 0.6 and 0.7); (6) dyeing time (in min) (10, 20, 30, 40, 50 and 60); (7) fixation time (in min) (15, 30, 45 and 60); (8) dyeing and fixation temperature (in °C) (40, 50, 60, 65,

70, 75); and (9) colour fixation agent (soda ash) concentration (expressed as colour fixation agent to cotton weight ratio) (see Table 2 for details).

#### The colour yield measurement

The colour yield of the dyed fabrics was measured by SF650 Spectrophotometer (DataColor International, USA). The face of the specimen was measured and the condition for measurement was set under specular excluded with large aperture. The fabric was folded two times for ensuring opacity. Illuminant  $D_{65}$  and standard observer of  $2^\circ$  were used. Three measurements were taken under the same parameters which were then averaged.

The colour yield expressed as K/S value from the wavelength of 400–700 nm with 10 nm interval within the visible spectrum was calculated by Eq. (1). The higher the K/S value, the more is the dye-uptake, resulting in better colour yield.

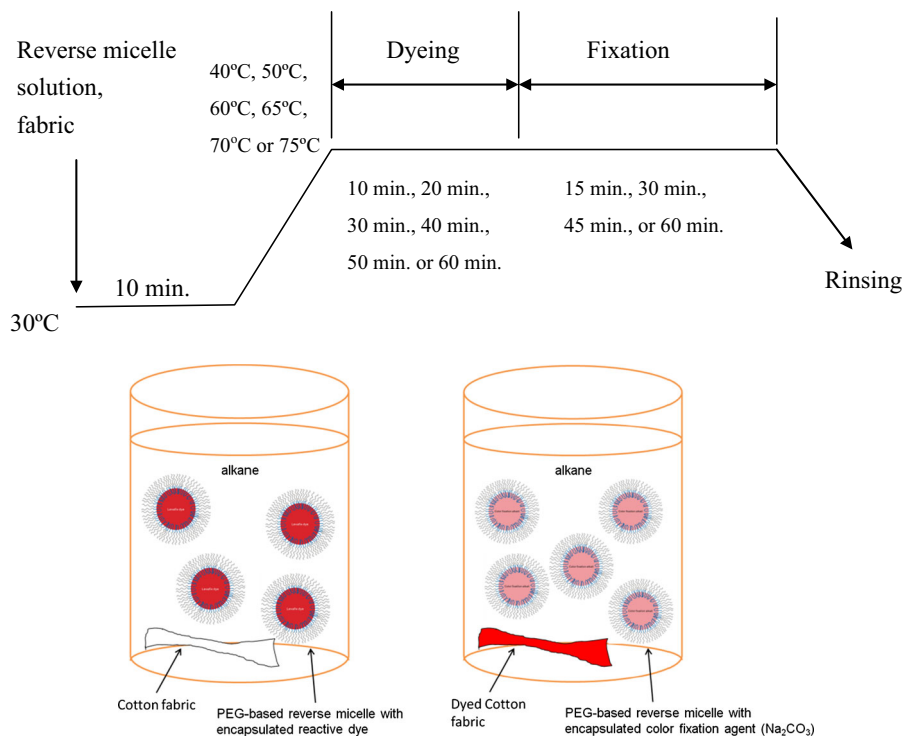
$$K/S = (1 - R)^2/2R \quad (1)$$

where K = absorption coefficient, depending on the concentration of colourant, S = scattering coefficient, caused by the dyed substrate, R = reflectance of the coloured sample.

#### Colour fastness to laundering

Colorfastness to laundering of dyed fabrics was evaluated according to AATCC Test Method

**Fig. 3** The flow of cotton dyeing and fixation process using reverse micelle approach in alkane without addition of salt



61-2013 (Colourfastness to Laundering: Accelerated) with Test No. 2A.

#### Scanning electron microscopy (SEM)

JEOL 5339F field emission scanning electron microscope (JEOL, Japan) equipped with an EDS (energy dispersive X-ray spectroscopy) system was used to capture high-resolution images of the surface of the cotton fabric.

#### Transmission electron microscopy (TEM)

TEM was employed to evaluate the morphology and encapsulation of reactive dye in reverse micelle. The dyes were first stained with an aqueous solution of 2 wt% uranyl acetate and air-dried overnight before TEM observation. Uranyl acetate selectively stained the carbonyl and sulphonate group present in reactive dye molecules and appeared darker than the surfactant phase in the TEM micrographs. TEM bright field imaging was performed on a JEOL 100 CX II microscope using 100 kV accelerating voltage.

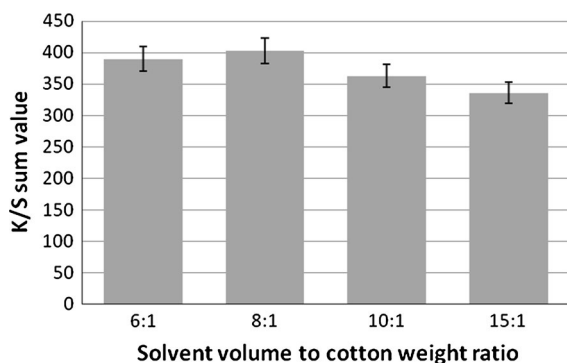
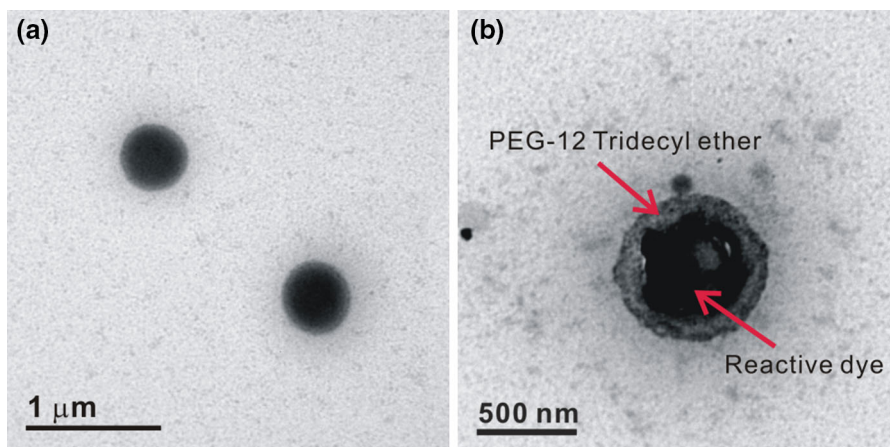
## Results and discussion

Figure 4 shows TEM images of reactive dye solution encapsulated within the interior region of reverse micellar system. Indeed, due to the soft texture of the material obtained at the extremely low pressure (required for TEM analysis), the sample exhibited a slight deformation in morphology of the spherical reverse micelle. Overall, the resulting reverse micelles are spherical in shape with average diameters of  $600 \pm 35$  nm and thickness of reverse micellar layer was about  $120 \pm 15$  nm. The images also showed that the particles were monodispersed and there were no signs of aggregation.

#### Effect of solvent volume to cotton weight ratio (solvent ratio)

Figure 5 represents the effect of solvent volume to cotton weight ratio (solvent ratio, v/w) on cotton dyeing with reactive dyes. The highest colour yield was measured at solvent ratio of 8:1, due to the proper distribution of dye. Low solvent ratio (6:1) may not be

**Fig. 4** TEM image of reverse-micelle encapsulated Levafix-CA dye with magnification of **a**  $\times 14,000$  and **b**  $\times 36,000$



**Fig. 5** Effect of solvent volume to cotton weight ratio on the colour yield (K/S sum value) (surfactant to co-surfactant mole ratio = 1:7; surfactant to water mole ratio = 0.05:1; water-pool volume for dye = 0.5 mL; water-pool volume for soda ash = 0.5 mL; dyeing time = 30 min; fixation time = 60 min; dyeing and fixation temperature = 60 °C; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)

sufficient for complete exposure of the fabric surface. At a higher solvent ratio of 15:1, dyes get aggregated in the form of a larger water-pool volume and the size of reverse micelle is too bulky to diffuse into cotton fibre matrix, resulting in a comparatively lower uptake of dye on the exposed cotton fabric surface area. The K/S sum value exhibits a declining trend as the bath ratio increases from 8:1 to 15:1.

#### Effect of surfactant to water mole ratio

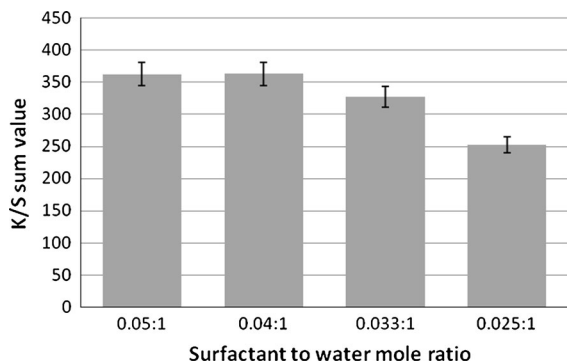
As indicated from Fig. 6, the highest K/S sum value is achieved at the surfactant to water mole ratio in the range of 0.05:1–0.04:1. A higher surfactant to water

mole ratio results in a highly stable water-pool encapsulation on cotton fibre surface during the dyeing process. When the amount of surfactant is reduced, the water-pool volume may not be well stabilised by the reverse micelle and some dyes can get aggregated and poorly dispersed in the solvent. The aggregation of dye induces a low diffusivity into interior region of cotton fabric.

Generally speaking,  $W_o$  (mole ratio of water to surfactant) can only affect the shape of the resultant reverse micellar structure synthesised by routine chemical methods via their effect on the structure of the microemulsion (the rigidity of the interface, the size of the water-pool, etc.). Reverse micelles are generally characterised by the molar ratio of water to surfactant  $S$ :  $W_o = [H_2O]/[S]$ . The micellar radius related with moles of surfactant and water per micelle. In this experiment, the value of the surfactant to water molar ratio ranged from 0.05:1 to 0.025:1 at fixed surfactant concentration. It is observed that at higher water to surfactant mole ratio results in better solubilisation of dye molecules and generates larger size of dye clusters encapsulated in single reverse micelle. This aggregation of dye molecules causes uneven dye-fibre surface interaction and can be easily washed off with low affinity to bind with cotton fabric.

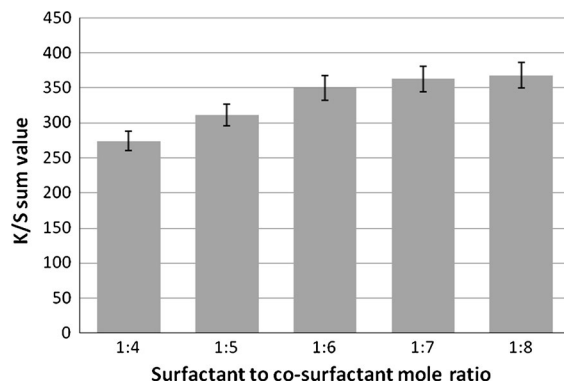
#### Effect of surfactant to co-surfactant mole ratio

Surfactant and co-surfactant are mainly located at the interface separating the water pool and the surrounding alkane to stabilize the mutual dispersion. A nonionic surfactant adsorbs strongly to an interface toward the



**Fig. 6** Effect of surfactant to water mole ratio on the colour yield (K/S sum value) (solvent volume to cotton weight ratio = 10:1; surfactant to co-surfactant mole ratio = 1:7; water-pool volume for dye = 0.5 mL; water-pool volume for soda ash = 0.5 mL; dyeing time = 30 min; fixation time = 60 min; dyeing and fixation temperature = 60 °C; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)

air or toward an organic phase because of its dual structure with a hydrocarbon segment chain with limited interaction with water (the hydrophobic part) and a polar group with strong interaction with water (the hydrophilic part). This interaction reduces the interfacial free energy. For surfactant concentrations above a certain limit in water (critical micelle concentration), the added surfactant self-assembles into the micelle structure. In the non-aqueous (organic) phase, the nonionic surfactant forms reverse micelles and the surfactant and the long chain alcohol are combined to stabilise the confined water-pool structure. The role of the co-surfactant together with the surfactant is to reduce the interfacial tension down to a very small value at which the interface is kinetically favourable to form ultra-small size and well dispersed droplets. The co-surfactant can act by inter-chelating between surfactant molecules at the interface between organic and aqueous phases. Thus, based on ability of the co-surfactant to affect the solvent properties, incorporation of co-surfactant with hydrocarbon chain length comparable to alkane chain length may eventually adjust Hydrophilic–Lipophilic Balance (HLB) and the curvature of the interface for effective water-pool partitioning characteristics. This indicates that the HLB value of the reverse micellar system is also decreased by further addition of *n*-octanol, because the HLB value of *n*-octanol (HLB = 5.1) is about 2.7 times lower than HLB value of poly(ethylene glycol) (12) tridecylether (HLB = 14). The solubility of *n*-octanol in water is low but completely miscible in



**Fig. 7** Effect of surfactant to co-surfactant mole ratio on the colour yield (K/S sum value) (solvent volume to cotton weight ratio = 10:1; surfactant to water mole ratio = 0.05:1; water-pool volume for dye = 0.5 mL; water-pool volume for soda ash = 0.5 mL; dyeing time = 30 min; fixation time = 60 min; dyeing and fixation temperature = 60 °C; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)

octane and thus *n*-octanol is well dispersed in octane. The solubilised *n*-octanol in the organic phase distributed along the micellar interface as well as in the bulk organic phase (octane) and the water-pool of the reverse micelles. Hence the *n*-octanol molecules contribute to the formation of reverse micelles as a co-surfactant. In other words, the micellar interfacial layers were made up of nonionic surfactant (poly(ethylene glycol) (12) tridecylether) and the co-surfactant (*n*-octanol) having their hydrophilic segment in contact with the water-pool region and the alkyl chains in the octane solvent. The optimisation of surfactant to co-surfactant weight ratio becomes important in stabilization of reverse micelle structure and effective encapsulation of dye clusters. The surfactant to co-surfactant weight ratio (1:8) in Fig. 7 reveals the highest K/S sum value. The results indicate that higher amount of *n*-octanol relative to the fixed surfactant amount relieved the stress at both sides of the micellar interfacial layers. Hence, it is considered that the hydrophobic chains of *n*-octanol (hydrocarbon groups) are responsible for the lower aggregation of reverse micelles. This result means that the incorporation of *n*-octanol molecules into the reverse micellar system may be used to control the distribution of dye on cotton fabric surface. Higher interfacial stabilities in reverse micelles are often associated with stable dye encapsulation. This study thus shows that the effect of co-surfactant to surfactant mole ratio can display high degree of dye-cotton fibre interaction if the micellar

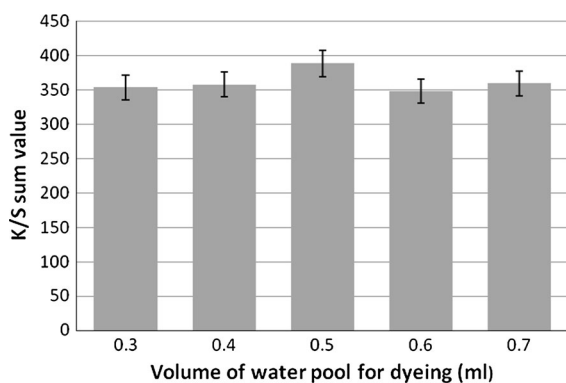


curvature and the rigidity of the micellar interfacial layers are changed.

#### Effect of water-pool volume in solubilisation of dye and colour fixation with soda ash

Since the size of reverse micelle is known to get enlarged as increasing quantities of water-pool volume are added (De and Maitra 1995), high concentration of dye can be highly solubilised in the swollen water-pool. An increase of poly(ethylene glycol) (12) tridecylether concentration also brings about an increase of maximum solubility of dye in the system. These results are relevant to an increase of total number of reverse micelle in the system.

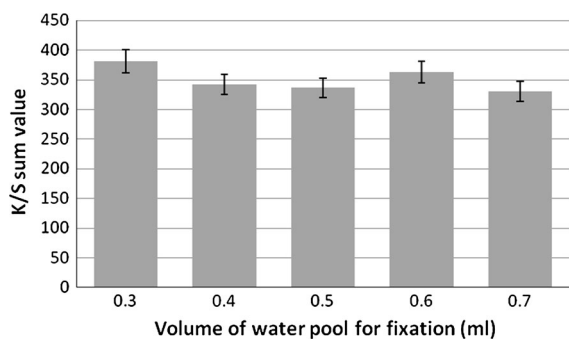
Figure 8 shows the results of dyeing of cotton fabric with reactive dye in reverse micellar system with varying volumes of total water pool. In this study, we have confirmed that variation of the amount of injected water has negligible influence on the K/S value because the amount of injected water is very small compared with that of alkane solvent. In order to compare the effect of dyeing in reverse micellar system, results of dyeing in aqueous system without addition of electrolyte are presented. The colour yield, K/S sum value, was calculated using the Kubelka–Munk equation in Eq. (1). As shown in Fig. 8, colour yields of fabrics dyed in reverse micellar system with total water-pool volume of



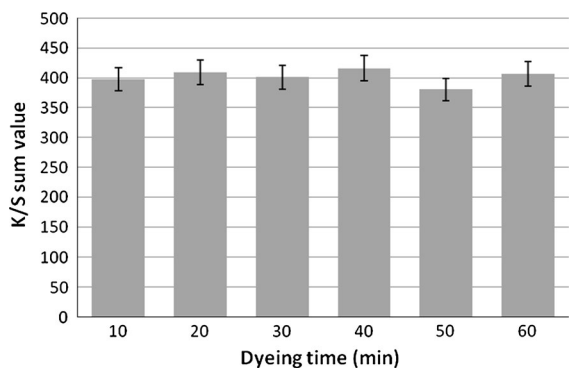
**Fig. 8** Effect of water-pool volume on the colour yield (K/S sum value) (Solvent volume to cotton weight ratio = 10:1; surfactant to cosurfactant mole ratio = 1:8; surfactant to water mole ratio = 0.033:1; water-pool volume for soda ash = 0.5 mL; dyeing time = 30 min; fixation time = 60 min; dyeing and fixation temperature = 60 °C; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)

0.5 mL are comparatively higher in the range from 0.3 to 0.7 mL. At low water-pool volume, cotton fibre may not be swollen adequately, resulting in insufficient formation of swelling of pores in the cotton fibre due to lack of free water. Thus, this limitation could inhibit the diffusion of reactive dye into the cotton matrix. As indicated from the results in Fig. 8, excess water-pool volume present in the system slightly weakens the dyeability when the fibre is swollen with water. The mole ratio of water to surfactant ( $W_o = [H_2O]/[S]$ ) value refers to solubilisation of water by surfactant. Increasing the water-pool volume implies that the  $W_o$  value tends to increase with concentration of surfactant. The increase in the  $W_o$  value corresponds to the decrease in the critical micelle concentration (cmc). This indicates that the solubilisation of water by surfactant is directly attributable to formation of reverse micelles using surfactant as the building block. Similarly, it is considered that the formation of reverse micelles affects the dispersibility of reactive dyes in water-pool. When reactive dyes are encapsulated in (poly(ethylene glycol) (12) tridecylether)-based reverse micelles, the resultant dyes are sufficiently dispersed on cotton fabric surface with the formation of undesired dye aggregates. Colour yield of cotton fabrics dyed in reverse micellar system is much stronger than those dyed in an aqueous system without addition of electrolytes. Aqueous dyeing media without electrolyte exhibits low capability to reduce electrostatic repulsion between dye and the fibre surface. In the reverse micellar system, 6 % reactive dye provides good solubilisation for the total volume of free water in water-pool (0.5 mL) and a desirable colour yield. These results clearly indicate that the reverse micellar system is able to maintain a high level of colour strength in dyed cotton fabric.

In both the aqueous and reverse-micellar systems, soda ash was employed as the colour fixation agent of reactive dye since it is commonly used in the conventional aqueous-based dyeing process. From the results in Fig. 9, the colour fixation efficiency of reactive dye in reverse micellar systems appears to be controlled by minimal water-pool content for solubilisation of colour fixation agent. The desired colour depth is observed under the water-pool volume of 0.3 mL for effective solubilisation of soda ash (Fig. 9).



**Fig. 9** Effect of water-pool volume on the colour yield (K/S sum value) (solvent volume to cotton weight ratio = 10:1; Surfactant to co-surfactant mole ratio = 1:8; Surfactant to water mole ratio = 0.033:1; water-pool volume for dye = 0.5 mL; dyeing time = 30 min; fixation time = 60 min; dyeing and fixation temperature = 60 °C; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)



**Fig. 10** Effect of dyeing time on the colour yield (K/S sum value) (Solvent volume to cotton weight ratio = 10:1; surfactant to co-surfactant mole ratio = 1:8; surfactant to water mole ratio = 0.04:1; water-pool volume for dye = 0.5 mL; water-pool volume for soda ash = 0.5 mL; fixation time = 60 min; dyeing and fixation temperature = 60 °C; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)

#### Effect of dyeing time

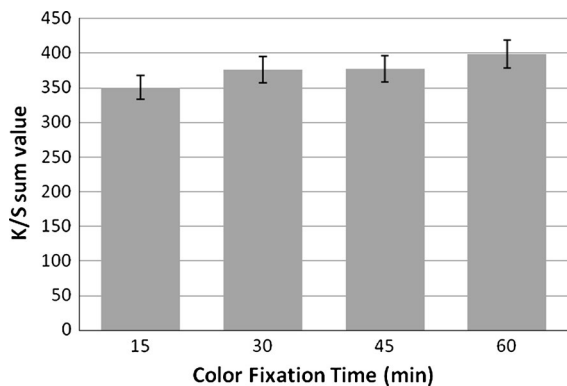
The maximum K/S sum value is observed when the dyeing time is between 20 and 40 min (Fig. 10). This indicates that the equilibrium dyeing can be achieved for cotton within 40 min at working temperature of 60 °C. It is found that when all other variables are kept fixed, with the increase in time of dyeing (10–60 min), K/S sum value is maintained in a range between 375 and 400. The maximum K/S sum value is achieved at 40 min. This may be explained by the possibility of achieving dyeing equilibrium at 40 min, depending on the rate of

dye diffusion (being the slowest step among transportation, absorption, diffusion and fixation of dye molecule). Reactive dye solubilised in the water-pool effectively migrates into the fibre due to the high dispersibility and sufficient mass transfer time in alkane solvent. On the other hand, dyeing rate of the cotton fabric dyed in alkane under the same conditions is lower than that of aqueous solution. These differences in K/S sum value can be attributable to the mass transfer time required for dye migration to the cotton surface. Short dyeing time (<10 min) does not fully activate dye molecules to migrate towards cotton fabric surface and results in extremely low colour yield. Similar results are also obtained when dyeing time is more than 40 min. Further extension of dyeing time, beyond 40 min also resulted in low colour yield. The reduction in colour yield is due to hydrolytic degradation of dye and the weak hydrolysed dye-fibre interaction.

#### Effect of colour fixation time

The fixation of reactive dye is determined by the covalent bonding between the dye and the fibre, which imparts good (colour) fastness in the end-uses. The colour yield and fixation efficiency after rinsing are often used for characterising the fixation of the reactive dye after complete removal of unreacted and hydrolysed dye in subsequent processes. In this work, the absorption of reactive dye by cotton fabric takes place without the presence of electrolyte in the PEG-based reverse micelle system and the colour is fixed using soda ash as the fixation agent.

As shown in Fig. 11, a longer colour fixation time increases the colour fixation efficiency as measured by the colour yield (K/S sum value). It is well known that reactive dye reacts with bulk water via hydrolysis competes with the formation of the covalent bond between dye and cotton surface (dye fixation reaction). The ratio of fixation to hydrolysis is determined by the extent of hydrolysis in the porous region of cotton fibres (Bird and Boston 1975). The effect of increase of soda ash added during the fixation stage is complex and usually involves an increase of the interaction probability between the dye and the cotton fibre. However, excess soda ash with more water-pool volume requirement may induce significant hydrolysis rather than fixation of the reactive dye, resulting in generation of poorly fixed reactive dye molecules. The adsorption and diffusion characteristics of the reactive dye in PEG-

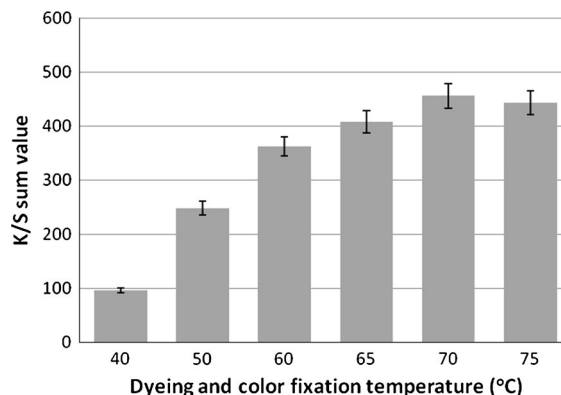


**Fig. 11** Effect of colour fixation time on the colour yield (K/S sum value) (Solvent volume to cotton weight ratio = 10:1; surfactant to co-surfactant mole ratio = 1:8; surfactant to water mole ratio = 0.04:1; water-pool volume for dye = 0.5 mL; water-pool volume for soda ash = 0.5 mL; dyeing time = 60 min; dyeing and fixation temperature = 60 °C; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)

based reverse micelle is considered as the major factor, as dye fixation in liquid-filled pores of the fibres is determined by the adsorption and diffusion of the dye through the textile fibre (Bird and Boston 1975). The equilibrium between the fixation and hydrolysis of the dye may also be affected by the dyeing medium. The cellulose ions produced in the water-pool of the micelle, with very limited ionisation, could be an inhibition factor for reducing the reaction between cotton fibre and reactive dye at the colour fixation stage. The fixation properties of reactive dye on cotton are improved by soda ash. Colour fixation in PEG-based reverse micellar systems is highly dependent on the alkali used, an effect which may be attributed to effectiveness of the solubilisation of dye in water-pool of the reverse micellar system. Generally speaking, properties of dye solubilisation in the non-ionic surfactant based reverse micelle are influenced by temperature, types of electrolyte, etc. Matijevic (1993) indicated that anions of salts are observed to have very small effect on solubilisation of aqueous phase in reverse micellar systems. The difference in anions of salts does not affect phase separation of the reverse micellar solution. As a result, more time is required to achieve the equilibrium of dyeing with reverse micellar system.

#### Effect of colour dyeing and fixation temperature

The effects of temperature in both dyeing and fixation processes are significant in terms of affinity of the dye



**Fig. 12** Effect of dyeing and colour fixation temperature on the colour yield (K/S sum value) (Solvent volume to cotton weight ratio = 10:1; surfactant to co-surfactant mole ratio = 1:7; surfactant to water mole ratio = 0.05:1; water-pool volume for dye = 0.5 mL; water-pool volume for soda ash = 0.5 mL; dyeing time = 30 min; fixation time = 60 min; dye concentration = 6 %; alkali to cotton weight ratio = 0.125)

on the cotton fibre. An increase in temperature affects reactivity of dye such as increased rate of hydrolysis and colour yield after the fixation process. However, temperature change intrinsically affects the rate of dyeing and dye migration from bath to fibre surface. Figure 12 shows that the optimal cotton dyeing and fixation temperature is 70 °C. When the dyeing temperature is 65–75 °C with soda ash as colour fixation agent, colour yield (K/S sum value) is around 400. At temperatures lower than 50 °C, the rate of dye migration to the fibre surface and the rate of dye penetration into fibre are both lower than the corresponding rate at the optimised temperature and the colour yield is approximately one-fourth of the optimal temperature of 70 °C. Dyeing at higher temperature causes better penetration of dye into fibre. However, dyeing temperature of 75 °C causes reduction in dye bath exhaustion as well as thermal degradation of reactive dye which results in slightly lower colour yield compared with 70 °C.

#### Effect of colour fixation agent (soda ash) concentration

The amount of colour fixation agent to cotton weight ratio depends on the dye concentration used in the dyeing process. The reactive dye is not solubilised in octane and is highly confined in an extremely small volume of water-pool. Each dye concentration in water-pool in a highly confined dye solution requires

**Table 3** The effect of colour fixation agent (soda ash) concentration at corresponding weight percentage of dyes (0.5, 1.5, 2.5 and 3.5 and 6 %) in terms of K/S sum value and

the optimised colour fixation agent to weight of cotton (w/w) under reverse micellar system

Dye concentration (% owf)	Colour fixation agent to cotton weight ratio (g/g)	K/S sum value	Optimised colour fixation agent to cotton weight (g/g)
0.5	0.02	35.52	0.06
	0.04	41.68	
	0.06	45.75	
1.5	0.06	131.33	0.08
	0.07	138.85	
	0.08	140.54	
2.5	0.08	218.14	0.085
	0.085	226.63	
	0.09	204.93	
3.5	0.09	308.51	0.095
	0.095	307.43	
	0.10	282.77	
6	0.115	395.51	0.125
	0.12	344.75	
	0.125	402.58	

Solvent volume to cotton weight ratio = 8:1; surfactant to co-surfactant mole ratio = 1:8; surfactant to water mole ratio = 0.05:1; water-pool volume for dye = 0.5 mL; water-pool volume for soda ash = 0.3 mL; dyeing time = 40 min; fixation time = 60 min; dyeing and fixation temperature = 60 °C

**Table 4** The optimised dyeing and colour fixation parameters using octane

Solvent volume to cotton weight ratio (v/w)	8:1					
Surfactant to co-surfactant mole ratio	1:8					
Surfactant to water mole ratio	0.04:1					
Volume of water-pool for dye (mL)	0.5					
Volume of water-pool for colour fixation agent (soda ash) (mL)	0.3					
Dyeing time (min)	40					
Fixation time (min)	60					
Dyeing and fixation temperature (°C)	70					
Dye concentration (% owf)	0.5	1.5	2.5	3.5	6	
Soda ash to liquor (g/L)	7.5	10	10.63	11.88	15.63	
Soda ash to cotton weight ratio (g/g)	0.06	0.08	0.085	0.095	0.125	

the optimal amount of colour fixation agent to cotton weight ratio to improve the colour fixation efficiency based on K/S sum value (Table 3).

The optimal dyeing and colour fixation process parameters

Based on the results, Table 4 summarises the optimum conditions of the reverse micelle dyeing system of cotton with octane as solvent.

It is well known that in aqueous medium, the adsorption of reactive dyes on cotton occurs by the charge interactions between hydrophilic dyes and hydrophilic surfaces. In terms of solubility of dyes, water has strong effect to solubilise reactive dyes due to its characteristics as a hydrophilic dyeing medium. Therefore, the solubilisation condition of dyes is a very important factor to determine adsorption in a non-aqueous exhaustion system such as non-polar hydrocarbon solvent. In this study, dye solubility in both

**Table 5** Colour yield

Colour	Dye concentration (% owf)	K/S sum value		
		Water	Heptane (%)	Octane (%)
Red	0.1	21.14	51.12 (↑141.82)	52.18 (↑146.83)
	1.5	71.17	152.86 (↑114.78)	139.81 (↑96.45)
	2.5	115.78	241.40 (↑108.50)	229.92 (↑98.58)
	3.5	153.81	289.02 (↑87.91)	296.58 (↑92.82)
	6	254.84	407.51 (↑59.91)	407.93 (↑60.07)
Yellow	0.1	20.78	32.77 (↑58.00)	30.01 (↑44.42)
	1.5	67.46	93.12 (↑57.70)	106.21 (↑57.44)
	2.5	99.50	139.76 (↑40.46)	141.70 (↑42.41)
	3.5	142.40	209.12 (↑46.85)	197.33 (↑38.57)
	6	197.74	280.81 (↑42.01)	261.79 (↑32.39)
Blue	0.1	29.26	38.00 (↑29.87)	31.86 (v8.89)
	1.5	94.15	114.11 (↑21.20)	98.61 (v4.74)
	2.5	154.15	177.44 (↑15.11)	159.02 (↑3.16)
	3.5	190.46	258.00 (↑35.46)	230.88 (↑21.22)
	6	300.56	335.78 (↑11.72)	308.24 (↑2.56)

aqueous and various alkane solvent media is also measured to determine the relationship with dye absorption capacity in terms of colour yield (K/S sum value) and dye concentration used in the dyeing experiment.

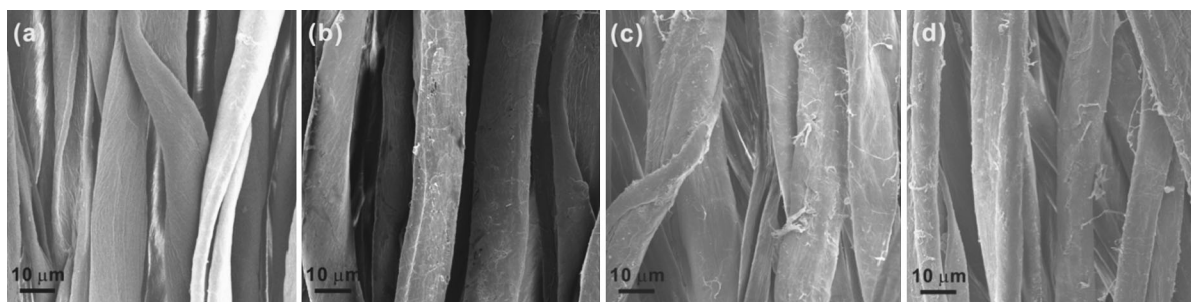
Table 5 shows that K/S sum values of fabrics dyed in heptane and octane are higher than fabrics dyed in aqueous solution (water). This is attributable to the dye solubility in water as the same dye concentration of reactive dye could be well dispersed in water with minimised volume; in the alkane system K/S sum values increase with the same order of magnitude as the aqueous system. It is concluded from these findings that when dye concentration in the confined aqueous solution (water-pool) increased, dye adsorption onto substrate increased dramatically. In alkane media, as shown in Table 5, the number of carbon atoms of hydrocarbon chain does not significantly influence adsorption and solubility. The dyeability of cotton fabric in heptane and octane based on measured colour yield (K/S sum value) is almost the same (Table 5). The reactive-red dye reveals the highest K/S sum value when compared with reactive-blue and reactive-yellow dyes with respect to dye concentration in the water-pool region. The higher K/S sum value indicates that reactive-red dye shows higher affinity than reactive-blue and reactive-yellow dyes under the same exhaustion conditions. Higher K/S sum value for reactive-red dyes can be attributed to the number of

available reactive groups and the degree of steric hindrance on reactive groups of the dye molecular structure.

Concentration of dye in the water-pool is one of the major factors for improving the fixation efficiency. The reactive dye is not solubilised in the bulk alkane medium—it is highly confined in an extremely small volume of water; even 6 % of dye encapsulated in water pool provides a highly confined dye solution to improve the dyeability based on K/S sum value.

Different from the general water-based dyeing process, the dyeing rate increased significantly in the reverse micelle based system due to the dye being highly concentrated in a confined water-pool volume. The highly concentrated dye in water-pool reveals a strong affinity to the fibre surface. Therefore, the rate of dye mass transfer to the cotton fibre surface is more efficient than that in aqueous system.

Cotton fabric shows stronger dye adsorption in PEG-based reverse micelle than in bulk water. The reason is that water solubilised in the interior of the reverse micelle has a relatively low polarity than the bulk water (Sawada and Ueda 2004; Kumar and Balasubramanian 1980), which leads to a lower degree of ionisation of the reactive dye molecule in the micellar core, thus reducing the repulsion force between the dye molecule and the fibre surface and enhancing the dye adsorption capacity.



**Fig. 13** SEM images of cotton fabric fibre surface (a) without dyeing; (b) dyeing in water; dyeing in reverse micellar system in (c) heptane and (d) octane, respectively

Based on Table 5, PEG-based reverse micellar dyeing system can achieve better dyeability than water-based dyeing. In the context of water consumption, water-based dyeing requires 50 mL water if 1 g of cotton (liquor-to-goods ratio is 50:1 in this study) is dyed (independent of dye concentration). However, in the PEG-based reverse micellar dyeing system, for 1 g fabric to be dyed with 6 % owf dye concentration, only 0.8 mL water is required. A large saving of water is achieved (save 98.4 % water). If liquor-to-goods ratio is 8:1 (which is the same as the solvent ratio used in this study), it will save 90 % water in the dyeing process.

Figure 13 displays SEM images of cotton fibre treated under different conditions. The SEM images highlight a disruption of the fibre surfaces of dyed cotton fibre (Figs. 13b–d) when compared with the smooth undyed fibre surfaces (Fig. 13a). Under SEM imaging, the observed images illustrate the ultrastructure of the dyed cotton fibres more clearly. The images of cotton fibre surface dyed in water (Fig. 13b) display similar tightly ordered fibrillar packing and smooth texture as seen in the undyed fibre samples (Fig. 13a). In case of alkane dyed cotton samples, microfibrils are loose and in random directions and the surface is observed to be microscopically rough due to disorderly placed fibres after immersion in heptane and octane. The generation of the microfibrils may be due to the use of low amount of water in the dyeing process.

#### Colour fastness to laundering

The colour change and staining results of the dyed samples are shown in Tables 6 and 7 respectively. The results in Table 6 indicate that there is no significant

**Table 6** Colour change results

Fabric sample (%)	Water	Heptane	Octane
Blue 0.5	4	5	5
Blue 1.5	4	5	5
Blue 2.5	4	5	5
Blue 3.5	4	5	5
Blue 6	4	5	5
Yellow 0.5	4	5	5
Yellow 1.5	4	5	5
Yellow 2.5	4	5	5
Yellow 3.5	4	5	5
Yellow 6	4	5	5
Red 0.5	4	5	5
Red 1.5	4	5	5
Red 2.5	4	5	5
Red 3.5	4	5	5
Red 6	4	5	5

Rating: 5 is the least colour change of original fabric; 1 is the most colour change of original fabric

change in colour when fabric samples were dyed in heptane or octane medium. However, when two dyeing systems are compared. The solvent-based (i.e. heptanes or octane) dyed fabrics achieves better colour retaining effect than water-based dyed fabrics. In case of staining, as the results shown in Table 7, the solvent-based dyed fabrics shows also better results than water-based dyed fabric. The water-based dyed fabrics would loss colour easily when compared with solvent-based dyed fabrics leading to poor colour change and staining properties. The easy loss of colour in water-based dyed fabrics may be due to dye hydrolysis during the dyeing process.

**Table 7** Staining results

	Fabric sample (%)	Rating of multifibre strips					
		Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
	Blue 0.5	4–5/5/5 <sup>a</sup>	4–5/5/5	4–5/5/5	4–5/5/5	4/5/5	4–5/5/5
	Blue 1.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/5/5	4–5/5/5
	Blue 2.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/5	4–5/5/5
	Blue 3.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/5	4–5/5/5
	Blue 6	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/4–5	4–5/5/5
	Yellow 0.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/5/5	4–5/5/5
	Yellow 1.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/5/5	4–5/5/5
	Yellow 2.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/5	4–5/5/5
	Yellow 3.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/4–5	4–5/5/5
	Yellow 6	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/4–5	4–5/5/5
	Red 0.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/5/5	4–5/5/5
	Red 1.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/5	4–5/5/5
	Red 2.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/5	4–5/5/5
	Red 3.5	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/4–5	4–5/5/5
	Red 6	4–5/5/5	4–5/5/5	4–5/5/5	4–5/5/5	4/4–5/4–5	4–5/5/5

Rating: 5 is the least staining in multifibre strip; 1 is the most staining in the multifibre strip

<sup>a</sup> Staining rating inside bracket indicates: water-based dyed sample/heptane-based dyed sample/octane-based dyed sample

## Conclusion

The nonionic surfactant-based reverse micelles were prepared with PEG-12 Tridecyl ether, *n*-octanol and alkane (heptane and octane) and optimised for dye absorption and fixation of reactive dyes on cotton fabric. The bath ratio, water-pool volume and initial dye concentration enhanced the amount of dye absorbed onto the fabric in the reverse micelle. Moreover, concentrated reactive dyes with minimised usage of water volume showed a better adsorption performance on cotton fabric in the PEG-based reverse micelle than in bulk water without the addition of electrolyte in the same conditions, mainly due to the strongly reduced ionisation effect between the reactive dye molecules and the cotton fibre, and the improved swelling of cotton fibre in the reverse micellar system. Furthermore, the higher colour fixation of dye was obtained when the optimal concentration ratio of dye and soda ash was used as the colour fixation agent in the reverse micelle. In summary, colouration of cotton fabric with reactive dye could be effectively carried out in the absence of electrolytes using PEG-based reverse micelle dispersed in alkane solvent as the dyeing medium. The dye absorption capacity in alkane media was found comparable with aqueous systems. As the number of carbon atoms of the alkane is 7 and 8, the amount of dye absorption increased with almost

the same order of magnitude as dyeing in aqueous system. In addition, the PEG-based reverse micellar dyeing system can save large amounts of water when compared with water-based dyeing (the water saving is depending on the liquor-to-goods ratio used).

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