Fibers and Polymers 2018, Vol.19, No.4, 894-904
DOI 10.1007/s12221-018-8061-y

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Effect of Hydrophilic-lipophilic Balance (HLB) Values of PEG-based Non-ionic Surfactant on Reverse Micellar Dyeing of Cotton Fibre with Reactive Dyes in Non-aqueous Medium

Alan Y.L. Tang[1], C.H. Lee[2], Y.M. Wang[1], and C.W. Kan[1]*

[1]*Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon 852, Hong Kong*
[2]*Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon 852, Hong Kong*

(Received January 25, 2018; Revised February 23, 2018; Accepted February 27, 2018)

Abstract: The effect of hydrophilic-lipophilic balance (HLB) of polyethylene glycol-based non-ionic surfactants of polyoxyethylene stearyl ether and polyoxyethylene tridecyl ether series of seven types on reverse micellar dyeing system of cotton was studied in non-aqueous heptane solvent medium. The relationships between HLB values of surfactants and reflectance, K/S_{sum} value and levelness of the dyed samples were investigated. The experimental results reveal that reflectance percentage increases and K/S_{sum} value decreases with increase of HLB value while good levelness and visual appearance of dyed samples can be achieved only with optimum HLB value. The most suitable HLB value for reverse micelle dyeing of cotton ranges from 12 to 14 since there is stable formation of reverse micelle under this range. Fastness to washing of dyed cotton samples was also evaluated. The results show that samples dyed by both non-ionic surfactant series can achieve excellent washing fastness supporting reproducibility of K/S_{sum} value, reflectance percentage and levelness of reverse micelle dyed samples with various surfactants.

Keywords: Cotton fibre, Hydrophilic-lipophilic balance, Non-ionic surfactant, PEG-based, Reactive dyeing, Reverse micelle, Non-aqueous medium

Introduction

Surfactant (S), which is an abbreviation for surface active agent, is characterised by its tendency to adsorb at surfaces and interfaces, a boundary between any two immiscible phases, with the driving force to lower the free energy of that phase boundary [1]. Surfactant molecules are amphiphilic, consisting of at least two parts, one of which is polar and soluble in a specific fluid (hydrophilic) while the other is nonpolar and insoluble (hydrophobic). Due to amphiphilic nature, surfactant molecules appear predominantly in monomeric form, with some fraction being adsorbed at system interfaces when surfactant concentration is less than a compound-specific threshold value [2]. When surfactant concentration is above the critical micelle concentration (CMC), surfactant molecules begin to self-assemble into ordered and colloidal aggregates to form micelles [3].

Micelles can be classified into normal micelles and reverse micelles. Normal micelles are surfactant aggregates spontaneously formed with hydrophilic head groups at the exterior and hydrophobic tails toward the center in water [4]. Reverse micelles are nanoscale spherical aggregates self-assembled by certain surfactants in non-polar media [5-7]. The structure of a reverse micelle can be typically represented as nano-sized droplet of a polar liquid phase, capped by a monolayer of surfactant molecules, and distributed uniformly within a non-polar oil phase (water-in-oil microemulsions) [8].

*Corresponding author: tccwk@polyu.edu.hk

In the reverse micellar system, the interaction of surfactant polar groups with polar solvent and the ability to solubilise a small amount of water in the interior region can result in the formation of a stable aqueous micro-environment (water pool) [9]. These isolated water pools can be regarded as nanoreactors where reactions take place as the micelles exchange reactants [10]. Numerous nanostructured materials, such as carbon quantum dots [11,12], gold nanoparticles [13], nanocrystals [14], protein nanoparticles [15] and silver nanoparticles [16] have been prepared by means of reverse micelle technique.

Reverse micelles are generally characterised by the molar ratio of water to surfactant (Wo): Wo=$[H_2O]/[S]$. They are aggregates containing a small amount of water (below Wo=15) whereas droplets containing a large amount of water molecules (above Wo=15) are regarded as microemulsions [17]. The curvature for reverse micelles corresponds to the energetically favourable packing configuration of surfactant molecules at the interface [18,19] and the micellar radius related with moles of surfactant and water per micelle.

Despite CMC and Wo, the change of Hydrophilic-Lipophilic Balance (HLB) value, which is the relationship or balance between the hydrophilic to the lipophilic portion of the nonionic surfactants [20], of surfactant has been shown to influence the size and stability of the polar core of the reverse micelles [21,22]. The concept of HLB was first presented by William C. Griffin, who later proposed formulae for calculation of HLB values of various non-ionic surfactants [23]. Pasquali *et al*. [24] claimed that HLB values of non-ionic surfactants were not well defined and the

HLB and required HLB values published by Griffin could only be taken as approximate guidelines. Recent research has analysed the importance of HLB value for coal dewatering [25] and preparation of essential oil nano-emulsions [26-29]. However, the importance of HLB value of nonionic surfactant on formation and application of reverse micelles in textile dyeing is still unknown.

Recently, lots of novel technologies have been introduced for dyeing or improving the dye ability of different types of fibres, such as sonochemical scouring for wool fibres [30], enzyme for polyamide fibres [31], natural mordant dyes [32], clay nanoadsorbent [33,34], chemical grafting of disperse dyes [35], nano-silica particles [36] and corona discharge surface ionization [37].

Apart from the above methods, the initial investigation on use of reverse micellar system in textile dyeing process was conducted by using anionic surfactant, named sodium bis-2-ethylhexlsulphosuccinate (Aerosol-OT, AOT) [38-41]. Since the ionic head groups of the surfactant in reverse micelles may adversely affect the polarity of the water-pool producing uneven micro-environment [42,43], nonionic surfactant, Triton X-100, has been investigated [44-46].

In our previous work, feasibility of dyeing cotton in heptane and octane solvent using polyethylene glycol (PEG)-based nonionic reverse micelles has been investigated and we found that good dyeing results can be achieved in the case of dyeing cotton with commercially available reactive dyes without the use of salt as a dye exhausting agent [47]. An attempt has also been made to investigate computerised colour matching and levelness of cotton dyeing with reactive dyes using PEG-based nonionic surfactant in solvent media [48]. However, both studies only used poly(ethylene glycol) (12) tridecylether ($C_{13}H_{27}(OCH_2CH_2)_nOH$) (n~12) with HLB=14 as the surfactant for the formation of reverse micelles. The effect of HLB value (below or above HLB=14) of surfactants on formation and application of reverse micelles in textile dyeing has not yet been studied.

This study has several objectives: (a) to examine dyeing of cotton samples with reactive dyes using nonionic surfactants of polyoxyethylene tridecyl ether series and stearyl ether series with different HLB values in heptane media; (b) to measure the colour yield and levelness of the dyed samples; (c) to compare the colour yield and levelness difference between dyed samples with similar HLB values of two different series and different HLB values within each series; and (d) to analyse the relationships between HLB value of non-ionic surfactants and the reflectance, absorption (K/S_{sum} value) and levelness of the dyed sample in reverse micelle heptane-based dyeing system.

Experimental

Materials

Ready-for-dyeing 100 % pure cotton interlock knitted fabric (40 wales per inch and 40 courses per inch) was used. The fabric was first cleaned with soap solution containing (2 g/*l* soda ash and 2 g/*l* soap) at temperature of 90 °C for 30 minutes. After washing, the fabric was rinsed with cold water and then dried at room temperature. Finally, the fabric was conditioned at relative humidity of 65±2 % and temperature of 20±2 °C for at least 24 hours prior to further experiment.

Preparation of PEG-based Reactive Dye Encapsulated Reverse Micelles

Three commercially-available reactive dyes (Levafix Yellow CA, Levafix Red CA and Levafix Blue CA dye, provided by DyStar, China) were used directly without further purification. The reverse micelles were prepared by a simple injection method at room temperature [47,48]. Several non-ionic surfactants with different HLB values, including polyoxyethylene stearyl ether series, also called Brij series (Brij S2, Brij S10, Brij S20 and Brij S100) ($C_{18}H_{37}(OCH_2CH_2)_nOH$), and polyoxyethylene tridecyl ether (PEG-TDE) series (Polyoxyethylene (10) tridecyl ether, poly(ethylene glycol) (12) tridecyl ether and poly(ethylene glycol) (18) tridecyl ether) ($C_{13}H_{27}(OCH_2CH_2)_nOH$), provided by Sigma Aldrich (Reagent Grade) were used to premix with co-surfactant (n-octanol) (Reagent Grade) with agitation. The HLB values of non-ionic surfactants are listed in Table 1. The surfactant to co-surfactant ratio used was 1:8 in mole ratio (1.49 m*l* co-surfactant per m*l* of surfactant). The surfactant/co-surfactant mixture was then dissolved in heptane solvent (Regent Grade with min. 99 % pure) to obtain organic surfactant solution to facilitate the self-assembly of reverse micelles. The solvent volume to cotton weight ratio used was 8:1 (8 m*l* solvent per gram of cotton). A controlled quantity of reactive dye aqueous solution was then added into the reverse micellar system dropwise. The dye concentrations in aqueous solutions prepared were 0.2 % (0.002 g dye per m*l* water), 1 % (0.01g dye per m*l* water), 3 % (0.03 g dye per m*l* water), 5 % (0.05g dye per m*l* water) and 7 % (0.07 g dye per m*l* water). The volume of dye solution added to the reverse micelle solution was

Table 1. The HLB values of non-ionic surfactants for the formation of reverse micelles

Non-ionic surfactant	Chemical formula	HLB value (from Sigma-Aldrich)
Brij S2	$C_{18}H_{37}(OCH_2CH_2)_2OH$	4.9
Brij S10	$C_{18}H_{37}(OCH_2CH_2)_{10}OH$	12
Brij S20	$C_{18}H_{37}(OCH_2CH_2)_{20}OH$	15
Brij S100	$C_{18}H_{37}(OCH_2CH_2)_{100}OH$	18
PEG-10	$C_{13}H_{27}(OCH_2CH_2)_{10}OH$	14
PEG-12	$C_{13}H_{27}(OCH_2CH_2)_{12}OH$	14
PEG-18	$C_{13}H_{27}(OCH_2CH_2)_{18}OH$	15

0.5 m*l*. After injecting the dye solution, the mixtures were vigorously stirred for 2 min until the well dispersed solution with reverse micelle encapsulated reactive dye was obtained.

Dyeing of Cotton Fabrics in Heptane-based Reverse Micellar Dyeing System

Five dyeing depths, 0.1 %, 0.5 %, 1.5 %, 2.5 % and 3.5 % o.w.f. (on-weight-of fibre) dye concentrations, were used. Dyeing of cotton fabrics was conducted at surfactant to water ratio of 1:25 in mole ratio (0.51 m*l* of water per m*l* of surfactant). The reverse micellar dye liquors were prepared by adding the corresponding quantities of surfactant, co-surfactant, dye solutions, heptane solvent and deionised water without addition of electrolytes. The dyeing profile and the amount of soda ash added in the heptane-based reverse micellar dyeing system are summarised in Figure 1 and Table 2 respectively. The cotton fabric was first immersed in reverse micellar dye liquor and the prepared dye liquor was poured into the shaking water bath at 30 ^{o}C with shaking for 10 min. The dyeing temperature was then increased to 70 ^{o}C at a rate of 2 ^{o}C/min. The dyeing process was conducted at 70 ^{o}C for 40 min. After dyeing, a controlled amount of soda ash aqueous solution (0.3 m*l*) was added into the dyeing bath and the fixation was conducted at 70 ^{o}C for 60 min. After fixation, the cotton fabric was immersed in soap solution (2 g/*l*) at 50 ^{o}C for 20 min twice. The fabric was then thoroughly rinsed with water, air-dried and conditioned at relative humidity of 65±2 % and 20±2 ^{o}C for at least 24 hours prior to further experiment.

Colour Yield Measurement

Colour yield of dyed fabrics using different HLB values of several non-ionic surfactants was measured by SF650 Spectrophotometer (DataColor International, USA). K/S values of dyed fabrics were measured in visible wavelength of 400 to 700 nm under the conditions of (i) specular included with large aperture (30 mm); (ii) opacity of the fabric was assured by folding the fabric two times; (iii) face of dyed fabric was measured; (iv) illuminant D65; and (v) standard observer of 10 ^{o}. Four measurements were taken under the same parameters which were then averaged.

The colour yield expressed as K/S value from the wavelength of 400 nm to 700 nm at 10 nm intervals within the visible spectrum was calculated by equation (1) [49] and the K/S_{sum} value was obtained by summing up K/S values at wavelengths of 400 nm to 700 nm. The higher the K/S value and its sum value, the more is the dye-uptake, and the better would be the colour yield.

$$K/S = (1 - R)^2/2R \tag{1}$$

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

Levelness Measurement

The relative unlevelness indices (RUI) are obtained by using reflectance values of the four randomly-selected spots on samples over the visible spectrum (λ=400-700 nm) at intervals of 10 nm. The measurement was conducted by SF650 Spectrophotometer (DataColor International, USA) using illuminant D_{65} under specular reflection and a standard observer of 10 ^{o} with a large aperture (30 mm).

The RUI mainly consists of four equations: (a) the standard deviation (s_λ) of reflectance values measured at a specific wavelength (equation (2)); (b) the uncorrected relative unlevelness index (RUI_u) (equation (3)); (c) the corrected relative unlevelness index (RUI_c) obtained by summation of coefficients of variation of the reflectance values (equation (4)); and (d) the relative unlevelness index (RUI) obtained by multiplying the coefficients of variation of reflectance by the photopic relative luminous efficiency function (V_λ) (equation (5)). The suggested interpretation of the RUI values is as listed in Table 3 [50].

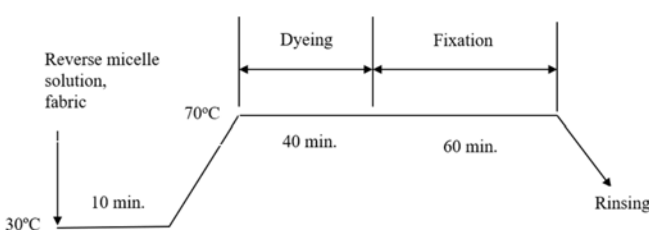

Figure 1. The workflow of cotton dyeing and fixation using heptane-based reverse micelle approach.

Table 2. Colour fixation agent (soda ash) concentration used

Dye concentration in fabric (% omf)	Colour fixation agent (soda ash) to cotton weight ratio (g/g)
0.1	0.060
0.5	0.060
1.5	0.080
2.5	0.085
3.5	0.095

Table 3. Suggested interpretation of the relative unlevelness index (RUI) values [50]

RUI	Visual appearance of levelness
<0.2	Excellent levelness (unlevelness not detectable)
0.2-0.49	Good levelness (noticeable unlevelness under close examination)
0.5-1.0	Poor levelness (apparent unlevelness)
>1.0	Bad levelness (conspicuous unlevelness)

$$s_\lambda = \sqrt{\frac{\sum_{i=1}^{n}(R_i - \overline{R})^2}{n-1}} \tag{2}$$

$$(RUI_u) = \sum_{\lambda=400}^{700} s_\lambda \tag{3}$$

$$(RUI_c) = \sum_{\lambda=400}^{700} s_\lambda / \overline{R} \tag{4}$$

$$RUI = \sum_{\lambda=400}^{700} (s_\lambda / \overline{R}) V_\lambda \tag{5}$$

CIEL*a*b* Measurement

The CIEL*a*b* of the dyed samples were measured by SF650 Spectrophotometer (DataColor International, USA) using illuminant D65 under specular reflection and a standard observer of 10 ^{o} with a large aperture (30 mm).

Colourfastness to Washing

Colourfastness to laundering of dyed fabrics was evaluated according to AATCC Test Method 61-2013 (Colourfastness to Laundering: Accelerated) with Test No. 2A.

Results and Discussion

Reflectance Curves of the Dyed Samples

Reflectance Curves of Brij Surfactant Series

Figures 2 to 4 depict reflectance curves of the three primary colours, yellow, blue and red respectively, of Brij surfactant series in different dye concentrations. Generally speaking, the reflectance percentage increases with increase of HLB value (positive relationship) when similar dye concentration is used. The samples dyed by using Brij S100 (HLB=18) obtain the highest reflectance percentage, followed by Brij S20 (HLB=15) and Brij S10 (HLB=12), while samples dyed by Brij S2 (HLB=4.9) obtain the lowest reflectance percentage. This indicates that among the Brij series, samples dyed by Brij S100 have paler shades than those dyed with Brij S20, Brij S10 and Brij S2. The possible reason is that there is no reverse micelle formation at high HLB value. Phase separation occurs which divides the dyeing medium into hydrophilic and hydrophobic layers without good dispersion of the solution [51,52]. Dye aggregate is also observed at the hydrophilic layer which indicates that there is no self-assembly of surfactant molecules into reverse micelle form so that it cannot function well as the dye carrier to carry the hydrophilic reactive dye molecules approaching to the surface of the fabric. However, this result does not mean that using Brij S2 can achieve the best dyeing effectiveness among the Brij series since reflectance is only one of the factors to be considered for evaluation of colour quality. The reflectance curves of dyed cotton fabrics by Brij series also reveal that no colour change occurred when different Brij surfactants with different HLB values are used since no shifting of reflectance curves is observed.

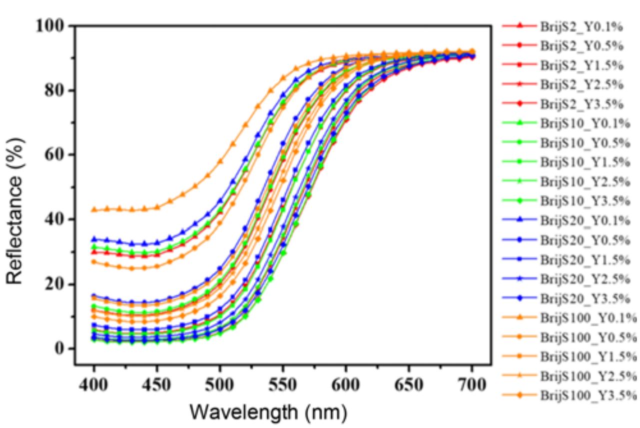

Figure 2. Reflectance curves of yellow colour of Brij surfactant series.

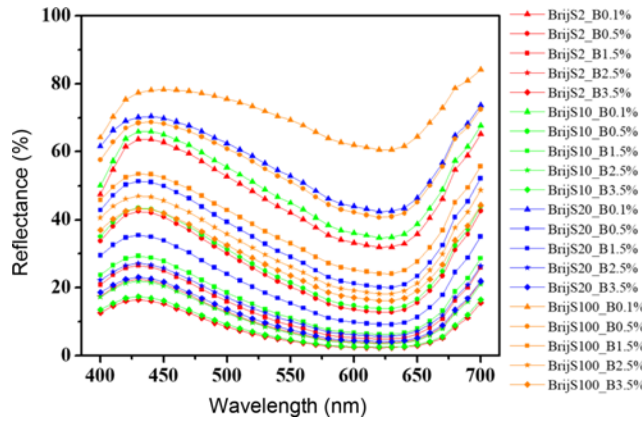

Figure 3. Reflectance curves of blue colour of Brij surfactant series.

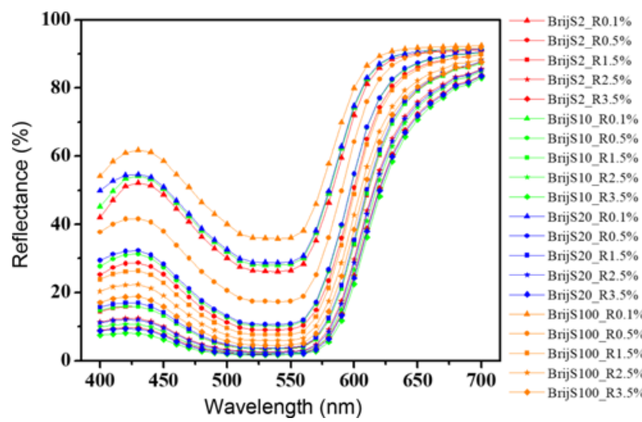

Figure 4. Reflectance curves of red colour of Brij surfactant series.

Reflectance Curves of PEG-TDE Surfactant Series

Figures 5 to 7 present reflectance curves of the three primary colours, yellow, blue and red respectively; PEG-TDE surfactant series were used in different dye concentrations.

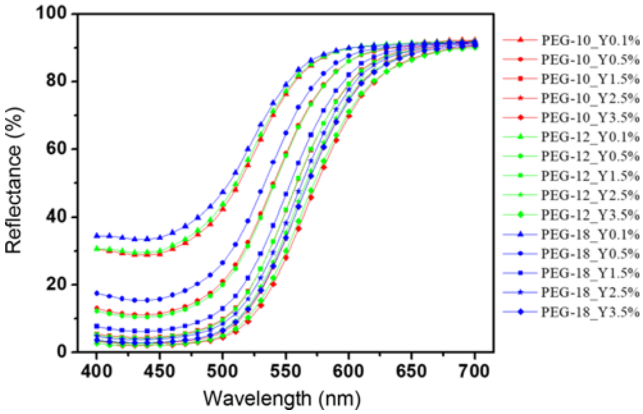

Figure 5. Reflectance curves of yellow colour of PEG-TDE surfactant series.

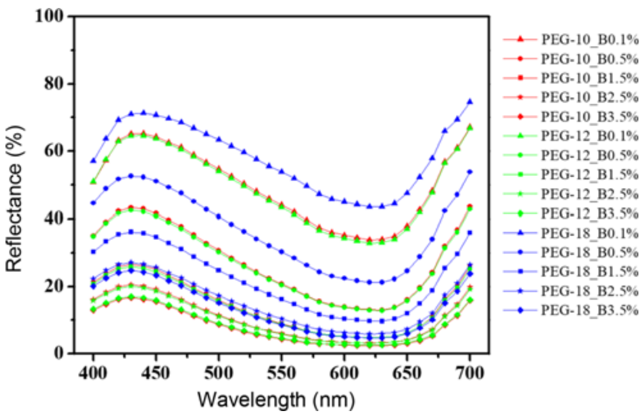

Figure 6. Reflectance curves of blue colour of PEG-TDE surfactant series.

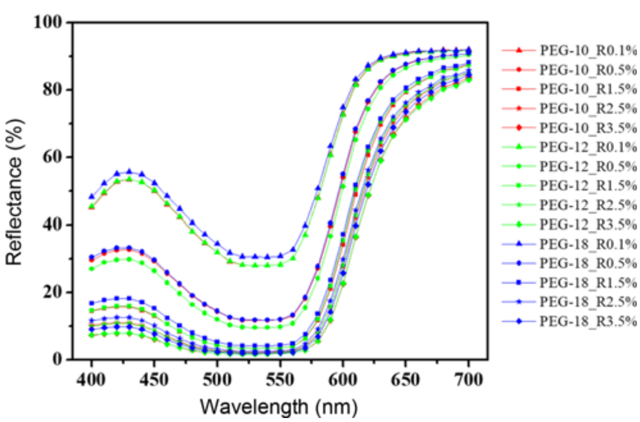

Figure 7. Reflectance curves of red colour of PEG-TDE surfactant series.

All the three colours produced by PEG-TDE surfactant series displayed phenomenon similar to that of the Brij series, in which the reflectance percentage increases with increase in HLB value. Since the HLB value of PEG-10 and PEG-12 (HLB=14) is nearly the same, it can be observed that the reflectance curve for each concentration of the dyed fabrics for all the three colours are nearly overlapped with each other. On the contrary, samples dyed by PEG-18 (HLB=15) have higher reflectance percentage, resulting in paler shade when compared with that of PEG-10 and PEG-12. The reflectance curves show no colour change and shift of the reflectance curves is observed which indicates that the surfactants (non-ionic) used do not affect the colour quality.

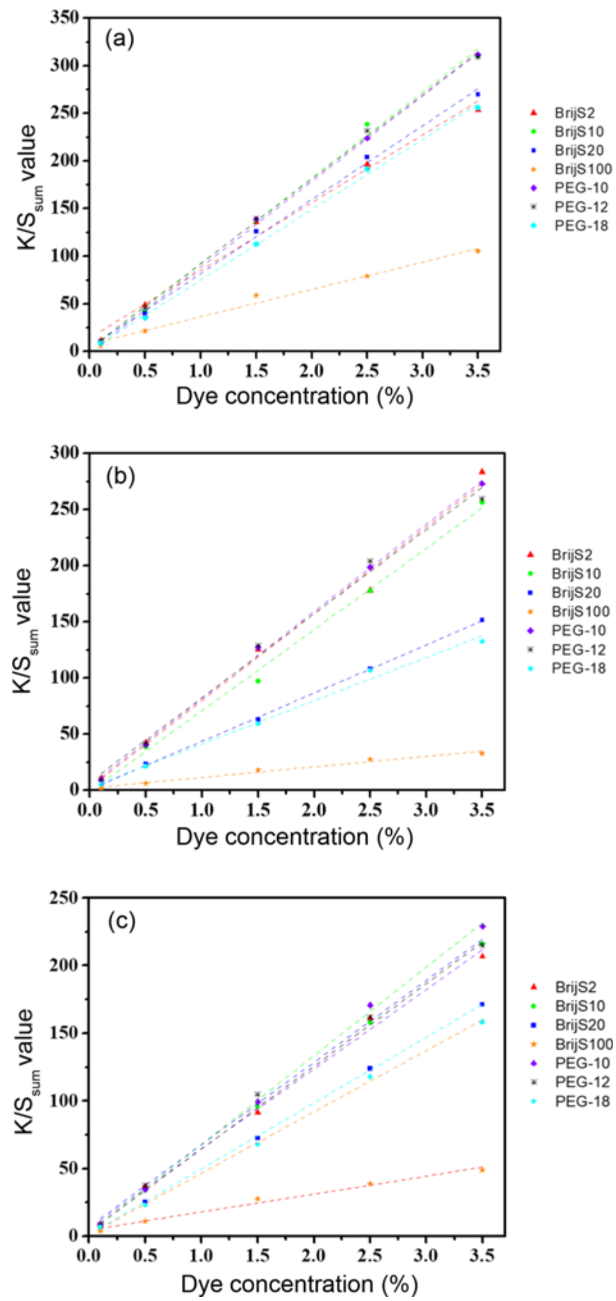

Figure 8. The K/S$_{sum}$ value of samples dyed by different surfactants in (a) red colour, (b) yellow colour, and (c) blue colour.

Comparison of Reflectance between Brij and PEG-TDE Surfactant Series

Comparison of reflectance percentage of Brij and PEG-TDE series shows Brij S100 > PEG-18 and Brij S20 > PEG-10 and PEG-12 > Brij S10 > Brij S2. This sequence shows the relationship that HLB value of surfactants is directly related to the reflectance percentage of the dyed cotton fabrics. Although different series of surfactants have different chemical formulae, Brij series ($C_{18}H_{37}(OCH_2CH_2)_nOH$) and PEG-TDE series ($C_{13}H_{27}(OCH_2CH_2)_nOH$), their non-ionic nature contributes to the consistency of colour production. The reflectance curves have no peak shifting even though Brij series possess more C and H atoms with higher hydrophobicity than that of the PEG-TDE series.

K/S_{sum} Values of the Dyed Samples

Figures 8(a) to (c) show K/S_{sum} values of dyed cotton samples in different dye concentrations, using different types of non-ionic surfactants. In general, the K/S_{sum} value increases with decrease in HLB value (negative relationship). The samples dyed by using Brij S100 (HLB=18) have the lowest K/S_{sum} value among the seven surfactants due to the presence of large dye aggregate and phase separation. The dye molecules cannot be well dispersed in the solution owing to the absence of reverse micelles as the carrier in heptane solvent dyeing medium. Moreover, it is observed that the residual dye left in the dye liquor after Brij S100 dyeing is much higher than in case of other surfactants, indicating that most of the dye molecules stay in the dye liquor rather than being diffused and absorbed in fibre.

Compared to Brij S20, PEG-18 dyed samples (both with HLB value of 15), have lower K/S_{sum} value for each dye concentration due to the presence of small dye aggregates found in the PEG-18 dye liquor after the dyeing process; these were not found in Brij S20. Therefore, the K/S_{sum} value of Brij S20 is slightly higher than that of PEG-18. However, owing to the second highest HLB value and the presence of much dye residue in the dye liquor, both Brij S20 and PEG-18 result in the second lowest K/S_{sum} value among the seven surfactants.

Among Brij S2 (HLB=4.9), Brij S10 (HLB=12), PEG-10 (HLB=14) and PEG-12 (HLB=14), the Brij S2 dyed sample seems to have the highest K/S sum value. The main reason is that there is nearly no dye residue left in the dye liquor; the after-dyeing solution observed is almost clear and transparent (Figure 9). However, in some dye concentrations, such as red 1.5-3.5 %, yellow 0.5-3.5 % and blue 1.5-2.5 %, the K/S_{sum} value of Brij S2 is lower than that of PEG-10 and PEG-12. In case of Brij S10, the K/S_{sum} value of dye concentrations of red 1.5-3.5 %, yellow 1.5 % and 3.5 % is also higher than that of Brij S2. This phenomenon can be explained by the instability (large fluctuation) of K/S_{sum} value of Brij S2 dyed samples in each measurement; the average of four measurements the K/S_{sum} value varies significantly.

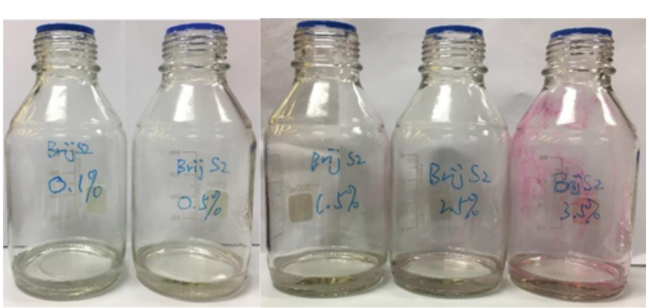

Figure 9. Photos of after-dyeing solutions of Brij S2 red colour.

Levelness of the Dyed Samples

The colour performance during use is one of the important factors in terms of expectations of the customers [53]. Colour levelness is a description of uniformity of the colour shade of the fabric [54,55]. The appearance of colour uniformity, in terms of levelness parameters in dyed fabrics and/or a union shade in dyed fabrics of more than one fibre type, is one of the important concerns in textile manufacturing industries [56]. To measure the colour levelness of dyed materials, an objective method, relative unlevelness index (RUI), which takes into account the coefficients of variation of reflectance measured over the visible spectrum with appropriate consideration of human vision sensitivity, was developed [50].

Tables 4 and 5 show RUI values and the visual assessment results of dyed cotton fabrics for Brij surfactant series and PEG-TDE surfactant series respectively. RUI value and visual appearance of the dyed samples are better with optimum HLB value of the surfactants. Brij S100 (HLB=18) and PEG-18 (HLB=15) dyed samples have good levelness because of the low absorption of dye molecules in fibre and high reflectance percentage, resulting in pale shade fabrics which in turn have comparatively better levelness than dark shade fabrics.

Although samples dyed by Brij S2 (HLB=4.9) seem to be darker in shade with low reflectance and high K/S sum value, the RUI value and the visual appearance of these dyed samples are the worst when compared with other surfactants due to low migration ability of dye molecules in phase separation dyeing condition.

Samples dyed with Brij S20 (HLB=15) have good to excellent visual appearance with reasonable RUI value. Compared with Brij S100 (HLB=18) and PEG-18 (HLB=15), there is no formation of dye aggregates in Brij S20 dyeing so that the dye molecules are well dispersed in the solution. Therefore, its K/S_{sum} value is also higher than that of Brij S100 (HLB=18) and PEG-18 (HLB=15). However, most of the dye remains in the dye liquor and therefore its K/S_{sum} value is not as good as that of Brij S10, PEG-10 and PEG-12.

Brij S10 (HLB=12) dyed samples also have good to excellent levelness due to the presence of reverse micelles as the dye carrier. There is no dye aggregation and phase separation observed during the dyeing process, contributing to its good levelness with reasonably high K/S_{sum} value.

To compare PEG-10 and PEG-12 with similar HLB value of 14, samples dyed by PEG-12 can achieve better levelness than PEG-10 partly due to the dyeing parameters used in this study following the optimisation work we have done on PEG-12 in a previous study [47]. After the optimisation, the colour yield and levelness of PEG-12 dyed samples can be greatly improved. To achieve good levelness in reverse micelle dyeing, the most determining step during the dyeing process is the addition of soda ash. It is observed that after addition of soda ash, the dye molecules diffuse into the fibre vigorously and the dyeing equilibrium is reached quickly. Step-wise control on soda ash addition with good shaking may be needed in large scale production.

Table 4. The relative unlevelness indices (RUI) and visual assessment of dyed cotton fabrics using Brij surfactant series

Sample	Brij S2		Brij S10		Brij S20		Brij S100	
	RUI	Visual	RUI	Visual	RUI	Visual	RUI	Visual
Red 0.1 %	0.20	Excellent	0.10	Excellent	0.11	Excellent	0.25	Good
Red 0.5 %	0.70	Poor	0.22	Good	0.16	Excellent	0.23	Good
Red 1.5 %	0.86	Poor	0.43	Good	0.19	Excellent	0.36	Good
Red 2.5 %	1.94	Bad	0.28	Good	0.36	Good	0.86	Poor
Red 3.5 %	0.50	Poor	0.30	Good	0.17	Excellent	0.51	Poor
Yellow 0.1 %	0.09	Excellent	0.03	Excellent	0.02	Excellent	0.02	Excellent
Yellow 0.5 %	0.14	Excellent	0.07	Excellent	0.03	Excellent	0.14	Excellent
Yellow 1.5 %	0.34	Good	0.11	Excellent	0.16	Excellent	0.28	Good
Yellow 2.5 %	0.08	Excellent	0.21	Good	0.21	Good	0.10	Excellent
Yellow 3.5 %	0.52	Poor	0.13	Excellent	0.10	Excellent	0.23	Good
Blue 0.1 %	0.26	Good	0.17	Excellent	0.04	Excellent	0.06	Excellent
Blue 0.5 %	0.67	Poor	0.40	Good	0.08	Excellent	0.15	Excellent
Blue 1.5 %	0.69	Poor	0.53	Poor	0.23	Good	0.30	Good
Blue 2.5 %	2.87	Bad	0.23	Good	0.23	Good	0.37	Good
Blue 3.5 %	1.68	Bad	0.35	Good	0.10	Excellent	0.24	Good

Table 5. The relative unlevelness indices (RUI) and visual assessment of dyed cotton fabrics using PEG-TDE surfactant series

Sample	PEG-10		PEG-12		PEG-18	
	RUI	Visual	RUI	Visual	RUI	Visual
Red 0.1 %	0.20	Excellent	0.10	Excellent	0.11	Excellent
Red 0.5 %	0.70	Poor	0.22	Good	0.16	Excellent
Red 1.5 %	0.86	Poor	0.43	Good	0.19	Excellent
Red 2.5 %	1.94	Bad	0.28	Good	0.36	Good
Red 3.5 %	0.50	Poor	0.30	Good	0.17	Excellent
Yellow 0.1 %	0.09	Excellent	0.03	Excellent	0.02	Excellent
Yellow 0.5 %	0.14	Excellent	0.07	Excellent	0.03	Excellent
Yellow 1.5 %	0.34	Good	0.11	Excellent	0.16	Excellent
Yellow 2.5 %	0.08	Excellent	0.21	Good	0.21	Good
Yellow 3.5 %	0.52	Poor	0.13	Excellent	0.10	Excellent
Blue 0.1 %	0.26	Good	0.17	Excellent	0.04	Excellent
Blue 0.5 %	0.67	Poor	0.40	Good	0.08	Excellent
Blue 1.5 %	0.69	Poor	0.43	Good	0.23	Good
Blue 2.5 %	2.87	Bad	0.23	Good	0.23	Good
Blue 3.5 %	1.68	Bad	0.35	Good	0.10	Excellent

CIE L*a*b* Value of the Dyed Samples

Within the CIE L*a*b* system, L* a* b* represent lightness, red-green axis and yellow-blue axis respectively. Tables 6 and 7 show the CIEL*a*b* value of dyed cotton samples by using Brij, water and PEG-TDE surfactant series. Generally speaking, the CIEL*a*b* value of dyed cotton samples by using Brij series, except Brij S100, and PEG-TDE surfactant series can achieve better results than the water-dyed samples. This means it is not practical and worthwhile to use surfactant with too high a HLB value (HLB=18) since dyeability of cotton in solvent medium without the formation of reverse micelles as the dye carrier is poor. Although the use of Brij S2 which has HLB value of 4.9 can achieve satisfactory results, levelness is one of the greatest problems that may adversely affect the aesthetic appearance of the dyed fabrics.

Table 6. The CIEL*a*b* value of dyed samples by Brij surfactant series

Sample (%)	Brij S2			Brij S10			Brij S20			Brij S100		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
Red 0.1	71.11	39.62	-4.86	71.88	39.14	-4.66	72.22	38.71	-4.72	76.23	33.95	-4.94
Red 0.5	54.76	56.54	0.50	57.77	54.44	-0.38	57.34	55.03	-0.80	64.80	47.63	-3.81
Red 1.5	46.12	59.88	5.70	44.65	61.47	7.16	45.95	61.28	6.01	54.38	57.47	1.03
Red 2.5	44.50	60.69	7.70	40.02	61.14	11.99	41.29	61.07	10.45	50.93	58.66	1.96
Red 3.5	39.94	60.70	12.98	37.26	59.80	15.68	38.58	60.28	13.32	47.15	60.22	5.24
Yellow 0.1	87.25	8.35	42.42	87.29	8.85	41.74	88.31	7.22	39.08	90.90	3.49	30.76
Yellow 0.5	79.75	21.16	65.26	79.71	21.14	64.75	81.73	18.31	59.77	86.03	11.30	48.11
Yellow 1.5	73.14	31.20	76.99	72.95	32.22	78.17	74.90	28.98	74.07	80.32	20.94	62.22
Yellow 2.5	68.73	37.27	81.16	68.94	37.46	81.67	70.12	35.68	79.48	78.64	23.39	64.52
Yellow 3.5	65.82	40.94	82.19	66.17	40.82	82.95	67.62	38.39	80.84	77.08	26.06	69.36
Blue 0.1	71.13	-4.85	-19.00	73.19	-4.72	-17.84	78.00	-4.88	-14.42	86.42	-4.27	-6.98
Blue 0.5	53.94	-3.94	-26.54	55.81	-4.14	-25.66	61.60	-4.50	-23.02	76.55	-5.06	-14.85
Blue 1.5	36.68	-0.61	-30.72	40.36	-1.95	-28.77	47.43	-3.43	-27.53	65.83	-4.69	-20.28
Blue 2.5	32.65	0.52	-30.45	33.81	-0.03	-30.40	39.89	-1.99	-28.67	59.46	-4.15	-22.63
Blue 3.5	24.78	3.60	-29.46	27.78	2.10	-29.89	35.59	-0.91	-29.52	56.41	-3.90	-22.69

Table 7. The CIEL*a*b* value of dyed samples by water and PEG surfactant series

Sample (%)	PEG-10			PEG-12			PEG-18		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Red 0.1	71.92	38.44	-4.58	71.93	38.49	-4.85	73.10	37.09	-4.40
Red 0.5	58.11	52.74	-1.12	56.52	54.73	-1.00	58.66	53.15	-1.35
Red 1.5	45.09	60.93	6.86	44.79	62.11	8.19	46.73	60.27	4.88
Red 2.5	40.92	61.24	11.98	41.28	61.76	12.18	41.75	61.35	10.47
Red 3.5	38.61	60.65	15.00	38.10	60.35	15.84	39.55	60.87	13.44
Yellow 0.1	87.31	8.94	43.29	87.88	7.88	41.64	88.65	6.77	37.92
Yellow 0.5	80.02	20.71	62.73	79.53	21.73	64.41	82.20	17.25	57.50
Yellow 1.5	72.03	33.37	78.92	72.40	32.42	78.43	75.14	28.70	72.94
Yellow 2.5	68.21	38.39	82.36	69.38	36.21	81.71	70.97	34.58	77.82
Yellow 3.5	65.11	41.71	81.99	66.34	39.77	82.67	68.76	37.30	80.44
Blue 0.1	72.53	-4.78	-18.23	72.34	-5.02	-18.36	78.69	-4.87	-13.96
Blue 0.5	53.72	-4.00	-27.17	54.42	-3.97	-25.84	63.28	-4.64	-22.71
Blue 1.5	37.32	-0.87	-30.81	37.41	-1.12	-30.12	48.22	-3.49	-27.18
Blue 2.5	32.03	0.75	-30.74	31.64	0.75	-30.23	38.60	-1.90	-27.64
Blue 3.5	27.34	2.50	-29.89	27.86	2.16	-29.75	37.35	-1.40	-29.31

Table 8. Colour change of dyed cotton with various surfactants

Specimen (%)	Colour change rating						
	Brij S2	Brij S10	Brij S20	Brij S100	PEG-10	PEG-12	PEG-18
Yellow 0.1	5	5	5	5	5	5	5
Yellow 0.5	5	5	5	5	5	5	5
Yellow 1.5	5	5	5	5	5	5	5
Yellow 2.5	5	5	5	5	5	5	5
Yellow 3.5	5	5	5	5	5	5	5
Blue 0.1	5	5	5	5	5	5	5
Blue 0.5	5	5	5	5	5	5	5
Blue 1.5	5	5	5	5	5	5	5
Blue 2.5	5	5	5	5	5	5	5
Blue 3.5	5	5	5	5	5	5	5
Red 0.1	5	5	5	5	5	5	5
Red 0.5	5	5	5	5	5	5	5
Red 1.5	5	5	5	5	5	5	5
Red 2.5	5	5	5	5	5	5	5
Red 3.5	5	5	5	5	5	5	5

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

Table 9. Colour staining of dyed cotton with various surfactants

Specimen (%)	Staining rating of multifibre strips					
	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Yellow 0.1	5/5/5/5/5/5/5[a]	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Yellow 0.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Yellow 1.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Yellow 2.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Yellow 3.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Blue 0.1	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Blue 0.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Blue 1.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Blue 2.5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5
Blue 3.5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5
Red 0.1	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Red 0.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Red 1.5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5	5/5/5/5/5/5/5
Red 2.5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5
Red 3.5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5	4-5/4-5/4-5/4-5/ 4-5/4-5/4-5

Rating: 5 is the least staining in multifibre strip; 1 is the most staining in the multifibre strip. [a]Staining rating inside bracket indicates: Brij S2 dyed sample/Brij S10 dyed sample/Brij S20 dyed sample/Brij S100 dyed sample/PEG-10 dyed sample/PEG-12 dyed sample/PEG-18 dyed sample.

Washing Fastness of the Dyed Samples

Tables 8 and 9 show the colour change and staining results of samples dyed by using Brij and PEG-TDE surfactant series respectively. The results reveal that the samples dyed by both series can achieve excellent washing fastness with no colour change and little to no staining after the test. This indicates that the unfixed dye residue is adequately removed away from the fabrics and the dye molecules left are covalently bonded with cotton.

Recommendation on HLB Value of Non-ionic Surfactants Used in Reverse Micelle Dyeing of Cotton

This study uses seven types of non-ionic surfactants from Brij series (Brij S2, Brij S10, Brij S20 and Brij S100) and PEG-TDE series (PEG-10, PEG-12 and PEG-18) to conduct reverse micelle dyeing of cotton fabrics in heptane solvent medium. Among these surfactants, the use of Brij S2 with too low HLB value of 4.9 may lead to phase separation which separates the dye liquor into two layers (hydrophilic dye layer and hydrophobic solvent layer) without formation of reverse micelle as the dye carrier. Using Brij S100 with too high HLB value of 18 may lead to formation of large dye aggregate in the dyeing process which may hinder the formation of reverse micelle and diffusion of dye molecules into the fibre. The use of PEG-18 and Brij S20 with HLB value of 15 may lead to low dye absorption so that more dye residual is produced after dyeing, increasing the amount of effluent discharge and the cost of effluent treatment. The most appropriate range of HLB values for reverse micelle dyeing of cotton is from 12 to 14 which includes Brij S10, PEG-10 and PEG-12 since this HLB range favours the formation of reverse micelle in stable spherical shape according to our previous work on TEM imaging of reverse micelle formed by PEG-12 [47]. The prepared dye liquor is clear and transparent which indicates good dispersion of dye molecules in reverse micelle. The reverse micelle thus can serve as the carrier to encapsulate the dye molecules approaching to cotton surface for further cotton-dye reaction. However, the use of non-ionic surfactant with HLB value of 14 may need optimisation on dyeing parameters so as to achieve good colour quality. Therefore, HLB value of 14 may be regarded as the upper limit for reverse micelle dyeing of cotton in heptane medium.

Conclusion

The effect of hydrophilic-lipophilic balance (HLB) values of PEG-based non-ionic surfactants of Brij and PEG-TDE series (total seven types) on reverse micellar dyeing system of cotton was studied in non-aqueous heptane solvent medium. The relationships between HLB values of surfactants and reflectance, K/S sum value and levelness of the dyed samples were investigated. The experimental results reveal that the reflectance percentage increased and K/S_{sum} value decreased with increase in HLB value while good levelness and visual appearance of dyed samples could only be achieved with optimum HLB value. Washing fastness of dyed cotton samples was also evaluated. The results showed that samples dyed by both non-ionic surfactant series could achieve excellent washing fastness supporting the reproducibility of K/S_{sum} value, reflectance percentage and the levelness of the reverse micelle dyed samples with various surfactants.

Acknowledgement

Authors would like to thank the financial support from The Hong Kong Polytechnic University for this work.

References

1. K. Holmberg, B. Jönsson, B. Kronberg, and B. Lindman, "Surfactants and Polymers in Aqueous Solution" 2nd ed. (K. Holmberg, B. Jönsson, B. Kronberg, and B. Lindman Eds.), pp.1-37, John Wiley & Sons, Ltd., England, 2003.
2. D. A. Edwards, R. G. Luthy, and Z. Liu, *Environ. Sci. Technol.*, **25,** 127 (1991).
3. X. Cui, S. Mao, M. Liu, H. Yuan, and Y. Du, *Langmuir.,* **24**, 10771 (2008).
4. J. L. Anderson, V. Pino, E. C. Hagberg, V. V. Sheares, and D. W. Armstrong, *Chem Commun.,* **19**, 2444 (2003).
5. D. Liu, J. Ma, H. Cheng, and Z. Zhao, *Colloid Surf. A-Physicochem. Eng.,* **135**, 157 (1998).
6. P. L. Luisi, *Angew. Chem.-Int. Edit.,* **24**, 439 (1985).
7. E. B. Leodidis and T. A. Hatton, in "Structure and Reactivity in Reverse Micelle" (M. P. Pileni Ed.), Vol. 22, p.270, Studies in Physical and Theoretical Chemistry, Elsevier, Amsterdam, 1989.
8. V. Uskoković and M. Drofenik, *Adv. Colloid Interface Sci.,* **133**, 23 (2007).
9. R. E. Riter, D. M. Willard, and N. E. Levinger, *J. Phys. Chem. B*, **102**, 2705 (1998).
10. J. H. Fendler, *J. Phys. Chem.,* **84**, 1485 (1980).
11. W. Kwon and S. W. Rhee, *Chem Commun.,* **48**, 5256 (2012).
12. H. Li, Z. Kang, Y. Liu, and S. T. Lee, *J. Mater. Chem.,* **22**, 24230 (2012).
13. K. Sun, J. Qiu, J. Liu, and Y. Miao, *J. Mater. Sci.,* **44**, 754 (2009).
14. K. Naoe, C. Petit, and M. Pileni, *Langmuir.,* **24**, 2792 (2008).
15. K. Naoe, S. Yoshimoto, N. Naito, M. Kawagoe, and M. Imai, *Biochem. Eng. J.,* **55**, 140 (2011).
16. H. Noritomi, Y. Umezawa, S. Miyagawa, and S. Kato, *Adv. Chem. Eng. Sci.,* **1**, 299 (2011).
17. M. Pileni, *J. Phys. Chem.,* **97**, 6961 (1993).
18. M. Kotlarchyk, J. S. Huang, and S. H. Chen, *J. Phys. Chem.,* **89**, 4382 (1985).
19. S. Safran and L. Turkevich, *Phys. Rev. Lett.,* **50**, 1930 (1983).
20. M. R. Housaindokht and P. A. Nakhaei, *Solid State Sci.,* **14**, 622 (2012).

21. M. M. Gacek and J. C. Berg, *J. Colloid Interface Sci.,* **449**, 192 (2015).
22. M. E. Parent, J. Yang, Y. Jeon, M. F. Toney, Z. L. Zhou, and D. Henze, *Langmuir.,* **27**, 11845 (2011).
23. R. C. Pasquali, N. Sacco, and C. Bregni, *Lat. Am. J. Pharm.,* **28**, 313 (2009).
24. R. C. Pasquali, M. P. Taurozzi, and C. Bregni, *Int. J. Pharm.,* **356**, 44 (2008).
25. B. Vaziri Hassas, F. Karakaş, and M. S. Çelik, *Int. J. Miner. Process.,* **133**, 97 (2014).
26. C. P. Fernandes, M. P. Mascarenhas, F. M. Zibetti, B. G. Lima, R. P. R. F. Oliveira, L. Rocha, and D. Q. Falcão, *Rev. Bras. Farmacogn.-Braz. J.,* **23**, 108 (2013).
27. W. C. Lu, D. W. Huang, C. C. R. Wang, C. H. Yeh, J. C. Tsai, Y. T. Huang, and P. H. Li, *J. Food Drug Anal.,* (2017).
28. M. H. Shahavi, M. Hosseini, M. Jahanshahi, R. L. Meyer, and G. N. Darzi, *Arab. J. Chem.*, http://dx.doi.org/10.1016/j.arabjc.2015.08.024 (2015).
29. S. Zhang, M. Zhang, Z. Fang, and Y. Liu, *Food Sci. Technol.-Lebensm.-Wiss. Technol.,* **75**, 316 (2017).
30. Y. Pan, C. J. Hurren, and Q. Li, *Ultrason. Sonochem.*, **41**, 227 (2018).
31. M. P. Gashti, R. Assefipour, A. Kiumarsi, and M. P. Gashti, *Prep. Biochem. Biotechnol.*, **43**, 798 (2013).
32. N. Baaka, A. Mahfoudhi, W. Haddar, M. F. Mhenni, and Z. Mighri, *Nat. Prod. Res.*, **31**, 22 (2017).
33. M. Parvinzadeh Gashti, B. Katozian, M. Shaver, and A. Kiumarsi, *Color Technol.*, **130**, 54 (2014).
34. M. Parvinzadeh Gashti, R. Rashidian, A. Almasian, and A. Badakhshan Zohouri, *Pigm. Resin. Technol.*, **42**, 175 (2013).
35. A. Peyravi, M. P. Gashti, and S. H. Hosseini, *Fiber. Polym.*, **15**, 2307 (2014).
36. M. P. Gashti, S. Moradian, A. Rashidi, and M.-E. Yazdanshenas, *Fiber. Polym.*, **14**, 743 (2013).
37. M. P. Gashti, I. Ebrahimi, and M. Pousti, *Curr. Appl. Phys.*, **15**, 1075 (2015).
38. K. Sawada and M. Ueda, *J. Biotechnol.*, **89**, 263 (2001).
39. K. Sawada and M. Ueda, *Dyes Pigments*, **58**, 37 (2003).
40. K. Sawada and M. Ueda, *Dyes Pigments*, **58**, 99 (2003).
41. K. Sawada and M. Ueda, *Color Technol.*, **119**, 182 (2003).
42. K. Sawada and M. Ueda, *J. Chem. Technol. Biotechnol.*, **79**, 369 (2004).
43. K. Sawada and M. Ueda, *J. Chem. Technol. Biotechnol.*, **79**, 376 (2004).
44. S. Yi, Y. Deng, and S. Sun, *Fiber. Polym.*, **15**, 2131 (2014).
45. S. Yi, Y. Dong, B. Li, Z. Ding, X. Huang, and L. Xue, *Color Technol.*, **128**, 306 (2012).
46. S. Yi, X. Tong, S. Sun, and F. Dai, *Fiber. Polym.*, **16**, 1663 (2015).
47. Y. Wang, C. H. Lee, Y. L. Tang, and C. W. Kan, *Cellulose*, **23**, 965 (2016).
48. A. Y. L. Tang, Y. Wang, C. H. Lee, and C. W. Kan, *Appl. Sci.*, **7**, 682 (2017).
49. J. H. Xin, “Total Colour Management in Textiles” (J. H. Xin Ed.), pp.136-159, Woodhead Publishing, UK, 2006.
50. C. Chong, S. Li, and K. Yeung, *J. Soc. Dye. Colour.*, **108**, 528 (1992).
51. W. C. Griffin, *J. Soc. Cosmet. Chem.*, **1**, 311 (1949).
52. W. C. Griffin, *J. Soc. Cosmet. Chem.*, **5**, 249 (1954).
53. W. Ingamells, “Colour For Textiles”, Society of Dyers and Colourists, 1993.
54. S. F. Ibrahim, D. Essa, and E. Osman, *Int. J. Chem.*, **3**, 11 (2011).
55. M. G. Uddin, “Study on the Color Levelness of Silk Fabric Dyed with Vegetable Dyes”, Vol. 3, p.10, Sustainable Chemical Processes, 2015.
56. Y. Yang and S. Li, *Text. Chem. Color.*, **25** (1993).