An Experimental Evaluation of

Non-ionic Surfactant Dehypon® LS54

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Abstract

Dehypon® LS45 (LS45) is a common non-ionic surfactant used by UK textile conservators, however it has very low cloud point of 20 ℃ which makes the temperature hard to control below the cloud point during wet cleaning. This research investigated the critical micelle concentration (cmc), the detergency and the effect of residues of an alternative surfactant Dehypon® LS54 (LS54). The cmc values of LS54 were found to be lower than that of LS45 when measured by Wilhelmy plate method and simplified drop weight method. Artificially soiled (carbon and olive oil) cotton and wool fabrics were washed with LS45 and LS54 and their detergency effects on the soils evaluated using colorimetry and visible spectrophotometry. The most effective concentration of LS54 for removing soils was found to be 0.3% w/v and its detergency effect was similar to LS45 at the same concentration. Surfactant residue was detectable on un-rinsed cotton and wool fabrics by Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs). DRIFTs analysis also proved that LS54 is more hydrophilic and has a longer fatty alcohol chain than LS45, which explains why it has a higher cloud point and cmc than LS45.

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Chapter 1

General introduction

1.1 Introduction

Synthetic surface-active agents (surfactants) have been widely used in textile conservation in the United Kingdom (UK). However one of the most widely used non-ionic surfactants, Synperonic® N (nonylphenol ethoxylate), was phased out within the EU in 2000 because of its bio-degradability which was felt to be responsible for various environmental issues. Following the situation, surfactant investigations into alternatives for Synperonic® N were carried out by the British Museum and the Victoria and Albert Museum (V&A).[1] They concluded that non-ionic Dehypon® LS45 (LS45; fatty alcohol with ethylene oxide and propylene oxide) would seem to be the best alternative and now it is widely used in the UK.

However, Dehypon® LS45 has a very low cloud point of 20 ℃ and is problematic in maintaining the temperature below its cloud point during wet cleaning. This has led to a search for yet another alternative non-ionic surfactant. A prospective surfactant is Dehypon® LS54 (LS54), whose cloud point is 30 ℃. It is currently used at

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[1] John A. Fields et al., "Finding Substitute Surfactants for Synperonic N," *Journal of the American Institute for Conservation* 43, no. 1 (2004): 55–73.

the V&A as a trial, whereas effects of detergency on textiles have not been examined

as carefully. This project has been designed to investigate LS54 and was initiated by a

suggestion from textile conservator, Frances Hartog, at the V&A, who was one of

several members conducting research to find a replacement for Synperonic® N ten

years ago.

In order to use LS54 as alternative for LS45, it is necessarily to know its cmc

value to determine the concentration of wash solution. If the cmc of LS54 is lower than

LS45, the amount of surfactants can be reduced for wet cleaning as surfactants are

used at between three and five times cmc. However recently, Dehypon's supplier

BASF has provided a much lower cmc value of LS45 (0.015 g/L) than the value which

has been understood and used for a long time around 10 years (0.598 g/L[2]). In addition,

these values are much lower than the reference cmc value of non-ionic surfactant

(0.05-0.5 g/L), known by textile conservators.[3] In addition to cmc value, the

detergency of surfactants is also an important factor in selecting appropriate

surfactants.

When wet cleaning is carried out, it must consider the possibility that some

surfactants may irreversibly absorb into fibres. In the field of textile conservation, little

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[2] Fields et al.,55-73.
[3] Ágnes Timár-Balázsy, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann
Series in Conservation and Museology (Oxford: Butterworth-Heinemann, 1998), 211.

research has been published about residues of surfactants on fibres, because it is analytically challenging and scientifically complex to detect very low concentrations of surfactant composing organic compounds on fabrics. Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs) is a very sensitive tool and, in principle, the recorded reflectance spectrum may be converted to an absorption spectrum appropriate for surface residue investigations. Over two decades, this technique has been applied for the identification of historical pigments and binders,[4,5,6] while limitations may well be a lack of case studies. It is considered that DRIFTs can help to address the issues of detecting low concentrations of surfactants on the woven fabric surfaces. The Chapter 6 is the conclusion of this dissertation.

1.2 Objective and the construction of each chapters

A major objective of this research was to address the current problem of low cloud point of LS45, by evaluating LS54 as the alternative non-ionic surfactant. By using the Wilhelmy plate method and simplified drop weight method, cmc of LS45 and

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[4] G. Hedley et al., "A Study of the Mechanical and Surface Properties of Oil Paint Films Treated with Organic Solvents and Water," *Journal of Thermal Analysis* 37, no. 9 (September 1, 1991): 2067–88, doi:10.1007/BF01905579.

[5] Carlos Eduardo Silva et al., "Diffuse Reflection FTIR Spectral Database of Dyes and Pigments," *Analytical and Bioanalytical Chemistry* 386, no. 7–8 (December 1, 2006): 2183–91, doi:10.1007/s00216-006-0865-8.

[6] Natalia Navas et al., "Benefits of Applying Combined Diffuse Reflectance FTIR Spectroscopy and Principal Component Analysis for the Study of Blue Tempera Historical Painting," *Analytica Chimica Acta* 630, no. 2 (23 2008): 141–49, doi:10.1016/j.aca.2008.10.008.

LS54 was determined for selecting concentration of wash bath. The detergency of artificially soiled cotton and wool was examined in order to discover the optimum condition for wet cleaning with LS54. This research also tried to develop an analytical method to determine any residue on fabrics by DRIFTs.

This dissertation is composed of 6 chapters. Chapter 1 introduces the background, the rational and the construction of this research. In Chapter 2, to establish the methodologies of this project, several aspects of LS54 were searched; namely, the chemical structure, the cmc, the effects of residues and their evaluation methods. Chapter 3 explained the result of the cmc values measured by the Wilhelmy plate method and simplified drop weight method. Chapter 4 gives the detergency of LS54 and LS45 on cotton and wool. In Chapter 5, as a new procedure for detecting surfactant residues, unsoiled cotton and wool with and without rinsing was analysed by DRIFTs. The Chapter 6 is the conclusion of this dissertation.

Chapter 2

Literature Review

2.1   Introduction

Chapter 2 explores in detail previous research in order to establish the methodologies

of this study. Section 2.2 covers properties and chemistry of surfactants, followed by critical

micelle concentration and cloud point of non-ionic surfactants. After comparing currently

used Dehypon® LS45 and a prospective non-ionic surfactant Dehypon® LS54 in section 2.4,

Sections 2.5 and 2.6 examine the effect of residues and analytical method for them.

2.2   Properties and chemistry of surfactants

Several authors have examined the chemical and physical principle of surfactants,

also called surface-active agents or detergents, in wet cleaning of historical textiles.[1,2,3,4,5]

In particular, Tímár-Balázsy provided a clear explanation and introduction of surfactants, as

well as many aspects of the chemistry of wet cleaning for textile conservators. The

surfactants are amphiphilic compounds with molecules having a hydrophilic (water

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[1] Judith H. Hofenk-De Graaff, "The Constitution of Detergents in Connection with the Cleaning of Ancient Textiles," *Studies in Conservation* 13, no. 3 (Spring 1968): 122–41, doi:10.2307/1505317.
[2] Judith H. Hofenk de Graaff, "Some Recent Developments in the Cleaning of Ancient Textiles," *Studies in Conservation* 27, no. Supplement-1 (Spring 1982): 93–95, doi:10.1179/sic.1982.27.Supplement-1.93.
[3] Ágnes Timár-Balázsy, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann Series in Conservation and Museology (Oxford: Butterworth-Heinemann, 1998), 194–213.
[4] Ágnes Tímár Balázsy, "Wet Cleaning of Historical Textiles: Surfactants and Other Wash Bath Additives," *Reviews in Conservation* 1 (2000).
[5] Mary Ballard, "Update: Detergency & the Aqueous Cleaning of Antique Textiles," *The Textile Speciality Group Postprints* 19 (2009): 95–96.

attracting) polar head and hydrophobic (water repelling) non-polar tail. They reduce the

surface tension of water by attracting hydrogen bonds of water molecules between the

hydrophilic head. The two major classes of surfactants used in conservation are anionic and

non-ionic. Anionic surfactants' hydrophilic heads, ionize to positively-charged cations,

while non-ionic surfactants do not ionize in water.[6] The choice of surfactant depends on its

suitability to the type of fibre and soiling.[7,8] It is considered that anionic surfactants are

more effective for cellulosic fibres, such as cotton and linen, whereas non-ionic surfactants

are used for proteinaceous fibres, such as wool and silk.[9,10] With regard to this point, the

most informative and in-depth reference is given by Walker.[11] It is said that ideally

proteinaceous fibres should be washed with non-ionic surfactants in the presence of weak

acids at pH values within their isoelectric range, approximately 4.5-5.5. In contrast,

cellulosic fibres should be washed in the presence of weak bases at pH values between 7

and 8.5. This is related to the chemical attraction between fibres and surfactants, and is

described on detail later.

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[6] Tímár Balázsy, "Wet Cleaning of Historical Textiles."
[7] Frances Lennard and Patricia Ewer, eds., *Textile Conservation: Advances in Practice*, Butterworth-Heinemann Series in Conservation and Museology (London: Elsevier/Butterworth-Heinemann, 2010), 143.
[8] Rebecca Tinkham and Nancy Kerr, "Effectiveness of Soil Removal by Two New Nonionic Surfactants, Orvus WA Paste, and Surfactant Blends" 11 (2001): 47–57.
[9] Centre for Textile Conservation, *Principles and Practice: Developing Skills Semester 2 Session: Detergency Handout* (MPhil Textile Conservation Course Handout, January 21, 2013).
[10] Jane Lewis and Dinah Eastop, "Mixtures of Anionic and Non‐ionic Surfactants for Wet‐cleaning Historic Textiles: A Preliminary Evaluation with Standard Soiled Wool and Cotton Test Fabrics," *The Conservator* 25, no. 1 (2001): 73, doi:10.1080/01410096.2001.9995166.
[11] David E. Walker, "Surfactants in Textile Conservation," in *The Textile Speciality Group Postprints*, ed. P. Ewer and B. McLaughlin, vol. 5 (presented at the AIC's 23rd Annual Meeting, St Paul, Minnesota: The Textile Speciality Group of AIC, 1995), 31.

2.3   Critical micelle concentration and cloud point

Each surfactant has optimum factors which maximise its performance. In particular,

critical micelle concentration (cmc) and cloud point are key values to note when using

surfactants in conservation wet cleaning.

In water, the surfactants' dual character of the amphiphile helps to form micelles with

the increase in concentration. The concentration which micelles form is called the critical

micelle concentration (cmc). Above the cmc, the surface tension no longer decreases even

by adding further surfactant (Fig. 2-1).[12,13] The cmc is the specific value of each surfactant.

Textile conservators usually use a detergent at between 3 and 5 times cmc, in order to wash

efficiently and also to rinse successfully.[14] Tímár-Balázsy quoted a typical cmc value of

non-ionic surfactant as being in the order of 0.05-0.5 g/l, whilst it should be updated with

the latest information indicates that some non-ionic surfactants have much lower cmc than

0.05 g/l. These values also depend on the analytical method of surface tension.

Cloud point is a temperature above which the solubility of a non-ionic surfactant

drops considerably and the solution becomes cloudy. It is considered that the hydrophilic

properties of non-ionic surfactant are conferred by the presence of oxygen atoms which are

capable of forming hydrogen bonds with molecules of water. As the temperature of the

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[12]   Ana Dominguez et al., "Determination of Critical Micelle Concentration of Some Surfactants by Three Techniques," *Journal of Chemical Education* 74, no. 10 (Spring 1997): 1227, doi:10.1021/ed074p1227.
[13]   Tímár Balázsy, "Wet Cleaning of Historical Textiles."
[14]   Centre for Textile Conservation, *Principles and Practice: Developing Skills Semester 2 Session: Detergency Handout.*

surfactant solution is increased, the hydrogen bonds gradually break causing the surfactant

to emerge from the solution at the cloud point. [15,16]
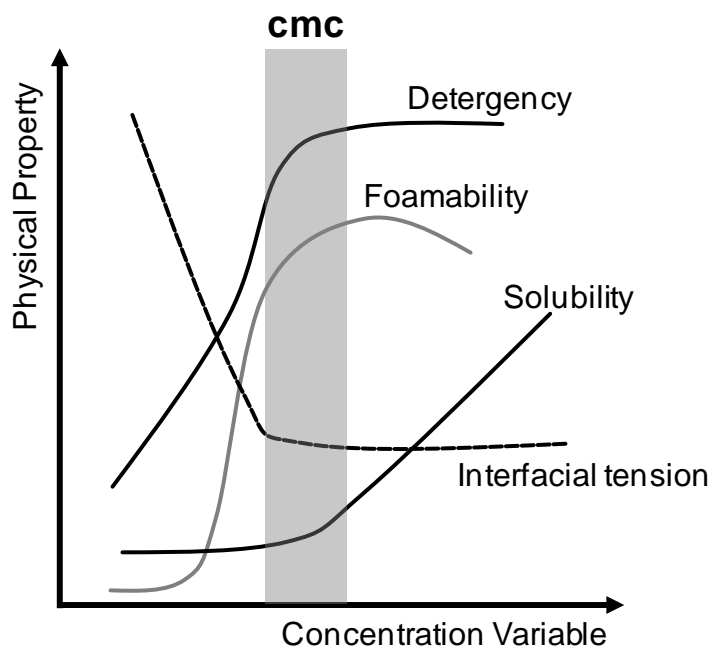
Fig. 2-1 Changes in surfactant solution properties as a function of concentration.
(Schematic figure taken and modified from Lange[17] and Wolbers[18])

2.4 Dehypon® LS45 and Dehypon® LS54

Fields et al.[19] conducted extensive experiments to find substitute surfactants for

Synperonic® N (nonylphenol ethoxylate) which had been widely used around the world

until banned due to its biodegradability causing environmental issues in 2000. They

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[15] Tímár Balázsy, "Wet Cleaning of Historical Textiles," 52.
[16] "Surfactants," accessed July 5, 2014,
http://www.essentialchemicalindustry.org/materials-and-applications/surfactants.html.
[17] K. Robert Lange, ed., *Detergents and Cleaners: A Handbook for Formulators* (Munich ; New York : Cincinnati: Hanser ; Distributed in the USA and in Canada by Hanser/Gardner, 1994), 6.
[18] Richard Wolbers, *Cleaning Painted Surfaces: Aqueous Methods* (London: Archetype Publications, 2000), 31.
[19] John A. Fields et al., "Finding Substitute Surfactants for Synperonic N," *Journal of the American Institute for Conservation* 43, no. 1 (2004): 55–73.

concluded that non-ionic Dehypon[®] LS45 would seem the likely alternative. Since then, Dehypon[®] LS45 has been widely used in the UK. However, Dehypon[®] LS45 has a very low cloud point of 20 ℃ and is problematic to maintain the temperature below its cloud point during wet cleaning. This leads to a search for yet another alternative non-ionic surfactant. A prospective surfactant is Dehypon[®] LS54 (fatty alcohol C_{12-14} with 5 moles of ethylene oxide and 4 moles of propylene oxide), whose cloud point is 30 ℃. It is currently used at the Victoria and Albert Museum as a trial, while effects of detergency on textiles have not been examined carefully.

Table 2-1 shows the chemical properties of LS45 and LS54 and their cmc values which has been used in textile conservation and recently provided by BASF.[20] Dehypon[®] LS45 is a fatty alcohol C_{12-14} with 4 moles of ethylene oxide (EO) and 5 moles of propylene oxide (PO), whereas Dehypon[®] LS54 is a fatty alcohol C_{12-14} with 5 moles of EO and 4 moles of PO. They are commercial surfactants which are available from BASF (Badische Anilin- und Soda-Fabrik) in Germany. Although BASF has not released detailed chemical structures, it is reported that the chemical structure of Dehypon[®] LS54 is $C_{12}H_{25}(OC_2H_4)_5(OC_3H_6)_4OH$ by US patent[21] and as determined by Juanssilfero et al.[22] by using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) (Fig. 2-2).

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[20] Personal communication (by e-mail) with BASF by the author and Frances Hartog, Victoria and Albert Museum in 2014.

[21] Michael Klinkhammer et al., "Hard Surface Cleaners Which Provide Improved Fragrance Retention Properties to Hard Surfaces," August 7, 2003.

[22] Ario Betha Juanssilfero et al., "Characterization of Copolymer Dehypon® LS 54 and Its Application for Aqueous Two-Phase Systems Paired with the Waxy Maize Starch for Protein Extraction," *International Journal on Advanced Science, Engineering and Information Technology* 1, no. 1 (2011): 65–71.

$$CH_3 - CH_2 \left[CH_2 \right]_9 CH_2 \left[O - CH_2 - CH_2 \right]_4 \left[O - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} \right]_5 OH$$

(a)

$$CH_3 - CH_2 \left[CH_2 \right]_9 CH_2 \left[O - CH_2 - CH_2 \right]_5 \left[O - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} \right]_4 OH$$

(b)
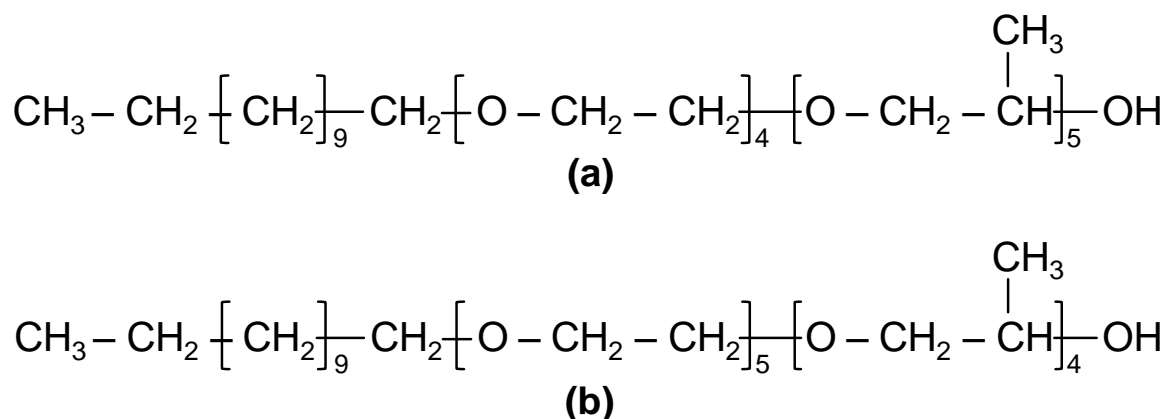
Fig. 2-2 The chemical structure of Dehypon® LS45 (a) and LS54 (b).
(LS54 is determined by Juanssilfero et al. [23] and LS45 is estimated by author.)

Table 2-1   The chemical properties and of Dehypon® LS45 and LS54.

	Dehypon® LS45	Dehypon® LS54
Chemical group	Fatty alcohol C_{12-14}, 4EO/5PO	Fatty alcohol C_{12-14} 5EO/4PO
Cloud point (ºC)	20 ºC	30 ºC
Current cmc (g/L)	0.598 [24]	Not reported
BASF's cmc (g/L) [25]	0.015	0.010

EO: ethylene oxide; PO: propylene oxide   BASF: Badische Anilin- und Soda-Fabrik

With regard to the cmc value, Dehypon's supplier BASF provides a much lower cmc value of Dehypon® LS45 (0.015 g/L) than the value which has been understood and used for a long time (0.598 g/L). In addition, these values are much lower than the reference cmc value of non-ionic surfactant (0.05-0.5 g/L), described in section 2.3.[26] Currently, Textile

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[23] Ario Betha Juanssilfero et al., 68.
[24] Sugden bubble method conducted by Field et al. in 2004.
[25] Personal communication (by e-mail) with BASF by the author and Frances Hartog, Textile Conservator at the Victoria and Albert Museum in 2014.
[26] Ágnes Timár-Balázsy, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann Series in Conservation and Museology (Oxford: Butterworth-Heinemann, 1998), 211.

Conservation Department at the Victoria and Albert Museum in London are using

Dehypon® LS45 at 2 g/L, and as a trial, Dehypon® LS54 at 1.3 g/L for wet cleaning.[27] Their

concentration of Dehypon® LS45 at 2 g/L is approximately 3.3 times cmc, which is based

on thecurrent cmc value 0.598 g/L. Since BASF's cmc is significantly lower, 1.3 g/L is

calculated from the ratio between BASF's cmc. According to their methodology, the

tentative cmc for Dehypon® LS54 is calculated as follow.

$$0.598 : \mathbf{X} = 0.015 : 0.010$$
$$\mathbf{X} = 0.598 \times \underline{\quad\quad}$$
$$\mathbf{X} = 0.39 \ (\text{g/L}) \qquad\qquad (\mathbf{X} = \text{Tentative cmc for Dehypon}^®\text{ LS54})$$

2.5   Effect of residue on fibres

The possibility that some surfactants may irreversibly absorb into fibres must be

considered. Surfactants penetrate into the lumen and the amorphous regions of cotton fibres

and into the cells of wool cortex with longer washing times and higher concentrations.[28] It

is considered that most of the anionic and non-ionic surfactant is not removed under

practical washing conditions as they are absorbed into the internal volume of the fibre.[29]

Furthermore, some anionic surfactants show irreversible bonding, called chemisorb, onto

proteinous fibres, such as wool and silk, caused by the chemical attraction between positive

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[27] Personal communication with Frances Hartog, Textile Conservator at the Victoria and Albert Museum in 1st April 2014.
[28] Walker, "Surfactants in Textile Conservation."
[29] G. N. Freeland, G. B. Guise, and I. M. Russell, "Sorption and Analysis of Some Nonylphenol Ethoxylate Surfactants on Wool," *Textile Research Journal* 55, no. 6 (June 1, 1985): 358–63, doi:10.1177/004051758505500605.

sites of the protein and negative charges of the surfactant.[30,31] It has been observed that

anionic surfactant, sodium lauryl sulphate (Orvus® WA Paste) which is widely used for wet

cleaning around the word, can absorb into wool at a pH below the isoelectric point to the

extent of 25 to 30% of the dry weight of the fibre.[32] Therefore, it is vital to select

appropriate surfactants to prevent the chemical interaction of the surfactant with textile

fibres. Because of a lack of substantivity to wool and silk compared with anionic surfactants,

non-ionic surfactants are used for proteinous fibres because they do not ionize in water and

can work efficiently in the isoelectric region of proteinous fibres.

2.6   Analysis of residues

In the field of textile conservation, little research has been published about residues of

surfactants on fibres, because it is analytically challenging and scientifically complex to

detect very low concentrations of surfactant composing of organic compounds on fabrics.

Rhee and Ballard examined residues of anionic surfactant, sodium lauryl sulphate (Orvus®

WA Paste) on silk by using SEM-EDS (SEM-Energy dispersive x-ray spectroscopy)

analysis and the methylene blue colorimetric method to determine the adsorption of sulphur

on the silk.[33,34] They reported that qualitatively silk does adsorb sodium lauryl sulphate. By

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[30] L. A. Holt and J. Onorato, "Substantivity of Various Anionic Surfactants Applied to Wool," *Textile Research Journal* 59, no. 11 (November 1, 1989): 653–57, doi:10.1177/004051758905901103.

[31] Walker, "Surfactants in Textile Conservation."

[32] H. Zahn, W. Stein, and G. Blankenburg, "Influence of Tensides on the Mechanical and Absorption Properties of Wool Fibers," *Textile Research Journal* 37, no. 8 (August 1, 1967): 701–3, doi:10.1177/004051756703700810.

[33] Heasoon Rhee and Mary W. Ballard, "The Chemical Interaction of Surfactants with Fibers, Especially

using the colorimetric test, it was found that the adsorption can be as high as 2.73%±0.3% owf (on weight of fibre). They concluded that there is a possibility of surfactant residue on silk, following a qualitative analysis. Several textile conservation students at the University of Glasgow tried to use Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy to confirm residues of surfactants after wet cleaning[35,36] but low concentrations and the diffuse reflective properties of the fibres made it difficult to detect surfactants on the woven fabric surfaces. Currently, there is no established analysis for the determination of residues of non-ionic surfactants on historical textiles.

Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs) can be used as an alternative method for investigating residues of surfactants on textile fibres. Popular in the nineties, this technique is now rarely used in the field of conservation. Hedley et al. analysed the surfaces of paintings before and after solvent cleanings using DRIFTs as a non-destructive tool in 1991.[37] Silva et al. provided a DRIFTs database of 25 dyes and pigments for the identification of unknown pigments used on historical and artwork artifacts in 2006.[38] Recently in 2008, Navas et al. tried to examine historic blue pigments and blue

Silk," in *Textile Specialty Group Postprints*, vol. 3 (presented at the AIC 21st annual meeting, Denver, Colorado, 1993), 28–37, http://www.bcin.ca/Interface/openbcin.cgi?submit=submit&Chinkey=164943.

[34] Heasoon Rhee and Mary W. Ballard, "Residues of Surfactant on Silk" 1 (1993): 327–29.

[35] Nora Meller, "A Preliminary Investigation into the Characterisation of Sooty Soilings on Historic Textiles" (MPhil Dissertation, Centre for Textile Conservation, University of Glasgow, 2013).

[36] Julie Benner, "Investigating the Potential of Decamethylcyclopentasiloxane (D5) as an Alternative Solvent for Textile Conservation Cleaning" (MPhil Dissertation, Centre for Textile Conservation, University of Glasgow, 2012).

[37] G. Hedley et al., "A Study of the Mechanical and Surface Properties of Oil Paint Films Treated with Organic Solvents and Water," *Journal of Thermal Analysis* 37, no. 9 (September 1, 1991): 2067–88, doi:10.1007/BF01905579.

[38] Carlos Eduardo Silva et al., "Diffuse Reflection FTIR Spectral Database of Dyes and Pigments,"

tempera paintings compared to modern samples. They could discriminate the historical samples as well as the presence of the binder.[39] Over two decades, this technique has been used for the identification of historical pigments and binders, while further examination might be limited by the lack of case studies.

DRIFTs is a very sensitive tool and, in principle, the recorded reflectance spectrum may be converted to an absorption spectrum appropriate for surface residue investigations. Textile fibres cause IR wavelengths to be reflected diffusely; that is to be scattered in all directions (Fig. 2-3). Consequently the IR beam penetrates only the top 0.5-2 µm of the surface.[40,41] Therefore, it is considered that DRIFTs can help to address the issues of detecting low concentrations of surfactants on the woven fabric surfaces.

(a) **(b)** **(c)**
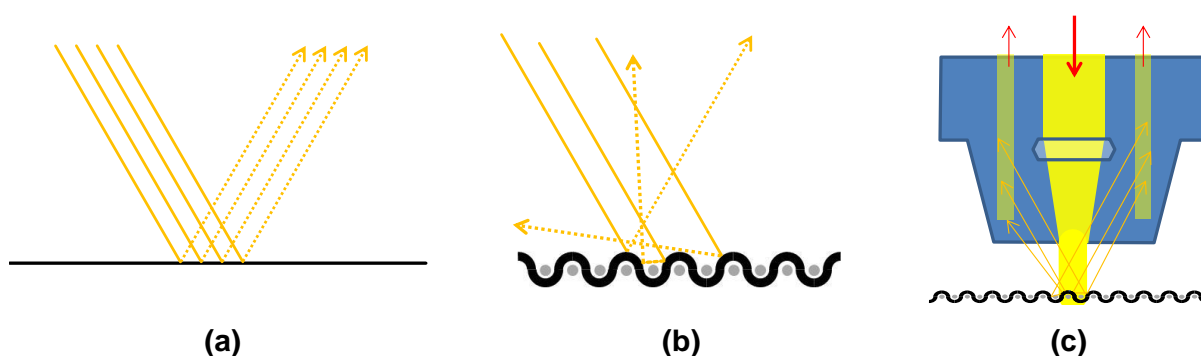
Fig. 2-3 Images showing different reflection types for IR light in ATR-FTIR (a), the diffuse reflectance effects of fibres on the IR beam (b) and DRIFTs technique collecting the scattered reflected light (c).

2.7   Conclusion

This literature review has provided the influence and rationale for this research project, by discussing research into the key factors of non-ionic surfactants.The emphasis is especially on their cmc and cloud point, the characteristics of Dehypon® LS45 and LS54, the effect of residues on fibres and the possibility of DRIFTs analysis for the conservation field. The importance of determining cmc value of Dehypon® LS45 and LS54 was emphasized as there is some confusion between the current value used in conservation and the supplier's cmc value. In addition, there is a lack of published research into, and case studies of, analysis of surfactant residues on textiles. Therefore, the following chapters will now examine this as well as evaluating the detergency of Dehypon® LS54.

Chapter 3

Determination of critical micelle concentration

3.1   Introduction

The aim of the experiment described in this chapter was to determine critical micelle concentration (cmc) of Dehypon® LS45 and LS54 by measuring dynamic and static surface tension and examine how these two values were different from the cmc of LS45 we have been used in textile conservation more than 10 years. In order to use LS54 as alternative for LS45, it is vital to know its cmc value to determine the concentration of wash bath. Furthermore, if the cmc of LS54 is lower than LS45, the amount of surfactants can be reduced for wet cleaning as surfactants are used at between 3 and 5 times cmc.

As described and investigated in Chapter 2, with increase of concentration of detergent, the surface tension is decreased at some point. This point is called as cmc. Every detergent has its own cmc value and above the cmc, the detergent works well. Textile conservators usually use a detergent at between 3 and 5 times cmc, in order to wash efficiency but also to rinse successfully. However recently, Dehypon's supplier BASF provides much lower cmc value of LS45 (0.015 g/L[1]) than the value which has been understood and used for a long time (0.598 g/L). In addition, these values are much lower than reference cmc value of non-ionic surfactant (0.05-0.5 g/L), given in Chemical Principles for Textile Conservation.[2] The cmc values of LS45 and LS54 are given in Chapter 2, Table 2-1.

In spite of the fact that textile conservators decide concentration of surfactant solutions on the basis of cmc value, little research has been published about determination of cmc in the field of conservation. This might be because it is analytically challenging, time

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[1] In this chapter, g/L was used rather than % w/v as it is a more common unit for determination of cmc. Measurement conversion table is given in Appendix 2.

[2] Ágnes Timár-Balázsy, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann Series in Conservation and Museology (Oxford: Butterworth-Heinemann, 1998), 211.

consuming and scientifically complex to understand surface physical chemistry of surfactants. Field et al. measured cmc of 12 non-ionic and anionic surfactants, including Dehypon® LS45, by the Sugden bubble method.[3] Tinkham and Kerr conducted the Du Noüy ring method for measuring cmc of Orvus® WA Paste (anionic), Synperonic™ A7 (non-ionic) and Triton™ XL-80N (non-ionic).[4] Takami also used the Du Noüy ring method to determine cmc of *Funori* solution as a detergent.[5] Rogerson demonstrated the calculation of a cmc value of a surfactant using a simplified drop weight method at an Icon (Institute of Conservation) workshop in 2007.[6] However, they did not mention why Sugden bubble method, Du Noüy ring method and drop weight method were selected in their experiments and demonstration.

The methods for determining surface tension fall into static and dynamic. Static testing measures the surface tension that is in equilibrium between the liquid surface and the bulk liquid. In contrast, dynamic methods measure the one that is in the process of being expanded or contracted.[7] A large number of methods have been applied to the determination of the cmc of surfactants. For instance, Wilhelmy plate and Du Noüy ring methods are techniques for static surface tension measurements whereas Sugden bubble method and drop weight method are utilized for dynamic surface tension studies.[8] In principle, dynamic surface tension is higher than static one.[9] It was found that cmc of LS45 provided by BASF was measured by

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[3] John A. Fields et al., "Finding Substitute Surfactants for Synperonic N," *Journal of the American Institute for Conservation* 43, no. 1 (2004): 55–73.

[4] Rebecca Tinkham and Nancy Kerr, "Effectiveness of Soil Removal by Two New Nonionic Surfactants, Orvus WA Paste, and Surfactant Blends" 11 (2001): 47–57.

[5] Mika Takami, "Funori as a Cleaning Agent for Historic Textiles: A Preliminary Investigation of Its Surfactant Properties and Cleaning Effect" (MA Thesis, The Textile Conservation Centre, University of Southampton, 2000), 49–50, 102–103.

[6] Cordelia Rogerson, *Why Conservators Need to Calculate a Cmc Value of a Surfactant*, Back to Basics Practical Workshop Life after Synperonic N': New Surfactants in Textile Conservation (The Textile Conservation Studio, The British Museum, October 15, 2007).

[7] W. Gale Cutler and R. C. Davis, eds., *Detergency: Theory and Test Methods*, Surfactant Science Series, v. 5 (New York, N.Y: Marcel Dekker, 1972), 635.

[8] Masatoshi Tikazawa and Kazuo Tajima, *Basic Chemistry Course: Surface Chemistry* (Maruzen, 2003), 23–27.

[9] Raj M. Manglik, Vivek M. Wasekar and Juntao Zhang, "Dynamic and Equilibrium Surface Tension of Aqueous Surfactant and Polymeric Solutions," *Experimental Thermal and Fluid Science* 25, no. 1–2 (2001): 63, doi:10.1016/S0894-1777(01)00060-7.

Du Noüy ring method (static method).[10] Therefore, it is considered that the differences of cmc values between current cmc used by conservation and BASF's cmc (see Chapter 2, Table 2-1) is due to the analytical method.

In the study reported here, the Wilhelmy plate method and simplified drop weight method were utilized for the determination of static and dynamic surface tension, respectively. It is believed that comparison of cmc values obtained from current experiment and previous research can be help to address the issue of the two different cmc values of LS45 and determine the cmc of LS54.

3.2 Experimental

3.2.1 Materials

Dehypon® LS45 was purchased from Conservation By Design Ltd. Dehypon® LS54 was supplied by BASF (Badische Anilin- und Soda-Fabrik) in Germany. Deionised water and ultrapure water (Millipore) were used for the drop weight method and Wilhelmy plate method, respectively.

3.2.2 Sample preparation

For the drop weight method, 2.5 g surfactant in 250 ml deionised water was prepared using a volumetric flask (10 g/L) as the stock solution. By volumetric pipette, 10 ml surfactant solution of the stock solution was measured and dissolved in 100 ml volumetric flask (1 g/L). As the same process, each concentration of solution (0.05-10 g/L) was prepared with a volumetric flask and volumetric pipette.

For the Wilhelmy plate method, 0.01 g surfactant in 100 ml ultrapure water was prepared using a volumetric flask (0.1 g/L) as the stock solution. Then, each concentration of

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[10] M. Schwarze et al., "Rhodium Catalyzed Hydrogenation Reactions in Aqueous Micellar Systems as Green Solvents," *RSC Advances* 1, no. 3 (September 9, 2011): 475–477, doi:10.1039/C1RA00397F.

solution (0.0001-0.1 g/L) was prepared with a volumetric flask and volumetric pipette from it.

3.2.3   Measurements

3.2.3.1   Drop weight method

The basic premise of the drop weight method is that surface tension can be calculated from physical drop characteristics as it forms at the end of a capillary tip of known external radius. The equation for surface tension calculation by drop weight is:

Fig. 3-1 The drop weight method illustrated.

$$mg = 2\pi r \gamma \times \varphi$$

$$\gamma = \frac{mg}{2\pi r} \times \varphi \qquad \text{Equation 1}$$

γ: Surface tension (mN/m)
m: Weight of the drop (g)
g: Gravitational acceleration (m/s^2)= 9.80665
r: The radius of the tip (mm)
φ: Correction factor (r/V$^{1/3}$, V: volume of the drop), called Harkins and Brown correction factor[11]

The drop-weight has been extensively used because of the applicable and accuracy in which measurements can be made. However, a major problem of drop methods is the determination of surface age. The surface age is generally taken to be the time interval from drop formation to drop detachment. Drop detachment is the result of the surface tension lowering due to surfactant diffusion to the surface. Surface age is a function of the measuring technique of the experimenter who must subjectively define the start of the surface that is the drop. In addition, Hommelen[12] found that subsequent drops were contaminated with residues

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[11] William D. Harkins and F. E. Brown, "A Simple Apparatus for the Accurate and Easy Determination of Surface Tension," *Journal of the American Chemical Society* 38, no. 2 (Spring 1916): 246–52, doi:10.1021/ja02259a007.
[12] Jacques R Hommelen, "The Elimination of Errors due to Evaporation of the Solute in the Determination of Surface Tensions," *Journal of Colloid Science* 14, no. 4 (1959): 385–400, doi:10.1016/0095-8522(59)90003-0.

from previous drops, and that drops with long surface ages were subject to evaporation effects.[13]

According to above theory, Rogerson demonstrated a calculation for the cmc value of a surfactant at the Icon workshop in 2007.[14] She simplified the above equation (1) to equation (2). The surface tension of each solution is calculated on the basis of the surface tension of deionised solution by weight.

$$\gamma = \gamma_w \times \frac{Wt\ (solution)}{Wt\ (water)} \quad \text{Equation 2}$$

γ: Surface tension (mN/m)
γ_w: Surface tension of water (mN/m);
(72.75 mN/m at 20 ℃, 74.23 mN/m at 10 ℃[15])
W: Weight of water

In this research, Rogerson's simplified drop weight method was used as it is more realistic and applicable method for textile conservators. This method cannot determine the exact value of cmc as the correction factor was not included in equation (2) and the shape of the burette's end was not straight. Therefore, the aim of conducting this method was to determine the apparent cmc value which can be helpful deciding concentration of surfactant solution for wet cleaning.

Fig. 3-2 (a) shows the simplified drop weight method experiment conducted at the Centre for Textile Conservation and Technical Art History (CTCTAH). Firstly, 50 drops of deionised water were delivered from a burette and weighed by an electronic balance. The drops should be emitted very slowly so that each forms into a round drop before it falls (Fig. 3-2 (b)). Then, each concentration of surfactant solution similarly delivered 50 drops slowly from the burette and weighed (Fig. 3-2 (c)). All drop weight measurements were repeated

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[13] Gail Masutani and Michael K. Stenstrom, "A Review of Surface Tension Measuring Techniques, Surfactants, and Treir Implications for Oxygen Transfer in Wastewater Treatment Plants" (Unpublished MA Thesis, University of California,, 1984).
[14] Rogerson, *Why Conservators Need to Calculate a Cmc Value of a Surfactant*.
[15] N. B. Vargaftik, B. N. Volkov, and L. D. Voljak, "International Tables of the Surface Tension of Water," *Journal of Physical and Chemical Reference Data* 12, no. 3 (July 1, 1983): 810, doi:10.1063/1.555688.

three times. Total time of measurements was approximately 13 hours (20 concentrations for two surfactants, repeated three times in each). By using the formula (1), the surface tension for each solution was calculated. As shown in Fig. 3-2, a drop of water formed more rounded and bigger (b) than surfactant solution (b) due to having a higher surface tension. As the weight of the drop (a) is larger than (b), they can be compared with equation (2). All experiments were carried out at room temperature (23 °C and 36-48%RH), while the solution of Dehypon® LS45 were cooled in refrigerator overnight at 10 °C and then immediately used around 10 °C at room temperature. However, there was the possibility that the temperature of the solution is increase towards 23 °C during the time of the experiment.
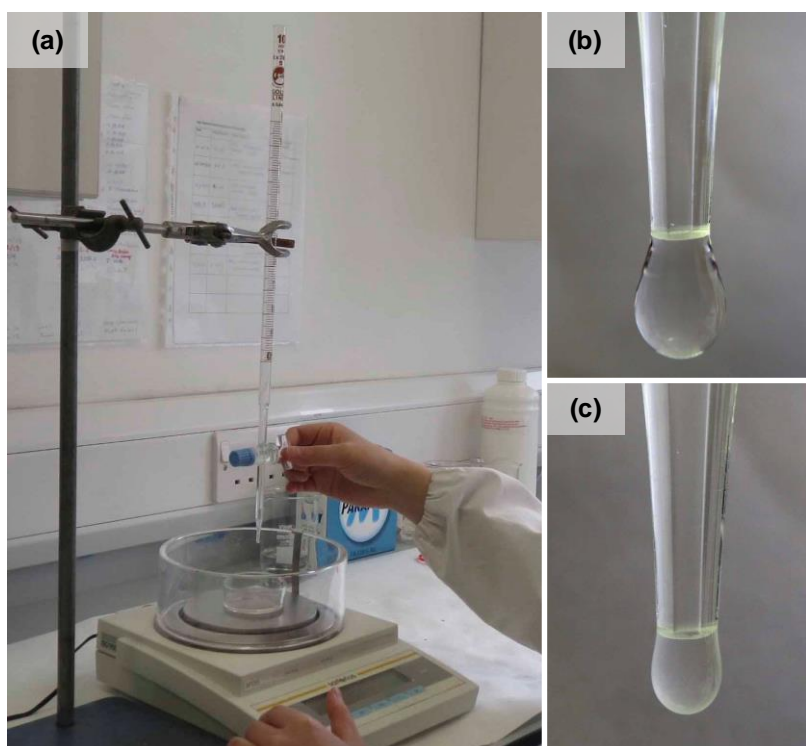
Fig. 3-2 Conducting the simplified drop weight method at the CTCTAH. (a): the equipment set up and creating a drop; (b): a drop of water; (c): a drop of surfactant.

3.2.3.2   Wilhelmy Plate method

The Wilhelmy plate method has been widely used for measuring static surface tension.[16, 17] Wilhelmy described this method in 1863 and it entails none of the correctional

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[16] E. Ramé, "The Interpretation of Dynamic Contact Angles Measured by the Wilhelmy Plate Method,"

factors described in the above drop method.[18] In this method, along the perimeter of the plate

the surface tension acts and the liquid pulls in the plate (Fig. 3-3). Then the plate detects the

pulling force (F) and determines the surface tension (γ) in equation (3). To ensure complete

wetting, the plate is usually made of micro-roughened platinum.[19]

$$\gamma = \frac{F}{L \cdot \cos\theta} \quad \text{Equation 3}$$

F: Force (mN), L: Perimeter of plate,
θ: Contact angle of plate and the liquid

Fig. 3-3 The image showing solution is measured by Wilhelmy plate method.[20]

Journal of Colloid and Interface Science 185, no. 1 (Spring 1997): 245–51, doi:10.1006/jcis.1996.4589.

[17] G. L. Gaines, "Surface and Interfacial Tension of Polymer Liquids –a Review," *Polymer Engineering & Science* 12, no. 1 (Spring 1972): 1–11, doi:10.1002/pen.760120102.

[18] Cutler and Davis, *Detergency*, 641.

[19] "Excellence in Surface Chemistry, Sigma Tensiometers," accessed August 14, 2014, http://files.instrument.com.cn/17img/old/literature/C10549.pdf.

[20] "Wilhelmy Plate Method," May 12, 2014, http://www.kruss.de/services/education-theory/glossary/wilhelmy-plate-method/.
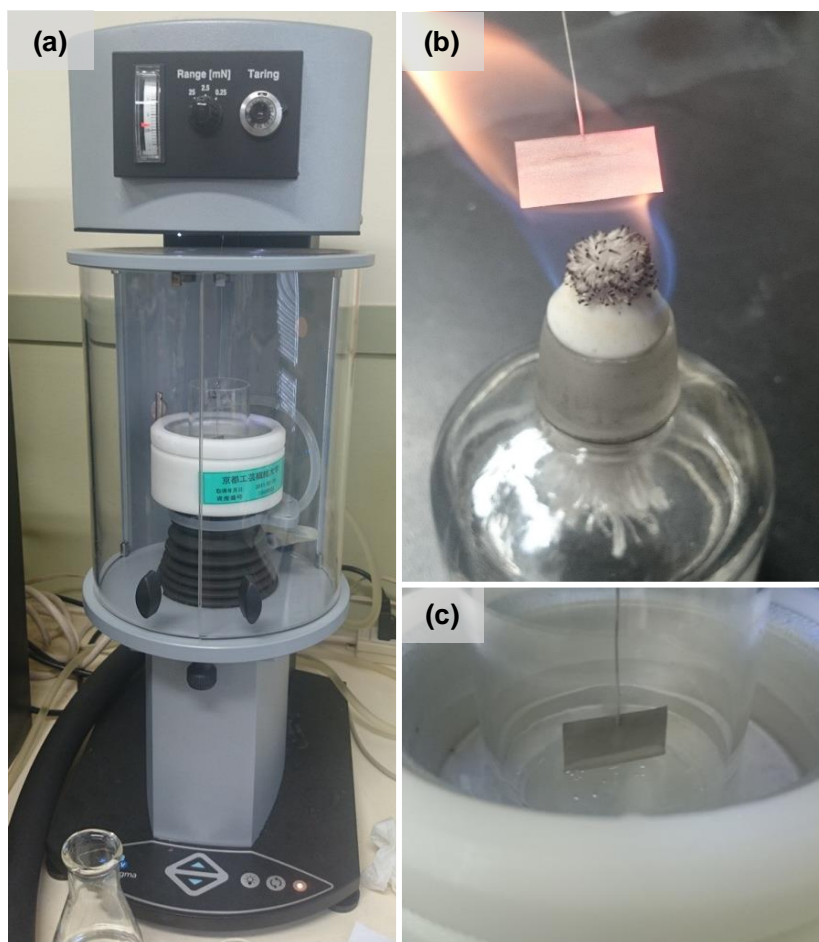
Fig. 3-4 The Wilhelmy plate method at the KIT in Japan. (a): equipment set up; (b): Burning the platinum (Pt) plate; (c): Detail of the Pt plate during measurement.

Surface tension measurements were conducted using the Wilhelmy plate method along with a KSV Sigma 700 automatic tensiometer (KSV Instruments Ltd., Finland) (Fig. 3-4 (a)) equipped with a temperature controller (EYELA NCB-1200). The testing was supported by PhD candidate Mr. Maeda under the guidance of Prof. Kawase at the Department of Chemistry and Materials Technology, Kyoto Institute of Technology (KIT) in Japan. The dimensions of the platinum Wilhelmy plate were 19.62 mm width, 10 mm length and 0.10 mm thickness. The platinum plate was cleaned with ultrapure water, and then burned in the flame of a spirit lamp before each experiment (Fig. 3-4 (b)). In each concentration of solution, 10 ml was pour in a glass beaker and set in a sample vessel (Fig. 3-4 (c)). The temperature in the sample vessel was controlled at 10 °C for LS45 and 25 °C for LS54. During the

measurements the platinum plate was immersed with a 5 mm immersion depth and then detached by the movement of a stage. The stage speed was 20 mm/min for all experiments. Measurement time ranged from 15 to 90 minutes. Fig. 3-5 gives an example of surface tension (mN/m) of 0.13 g/L and 0.013 g/L LS54 solution against time (seconds) gained in this experiment. Measurement was conducted until the value of surface tension beamed stable. The lower concentration of surfactant is, the longer time is needed for keeping equilibrium of the surface tension. Final three points of surface tension after the equilibrium were averaged and SD (Standard Deviation) was calculated in order to determine cmc value of surfactant.
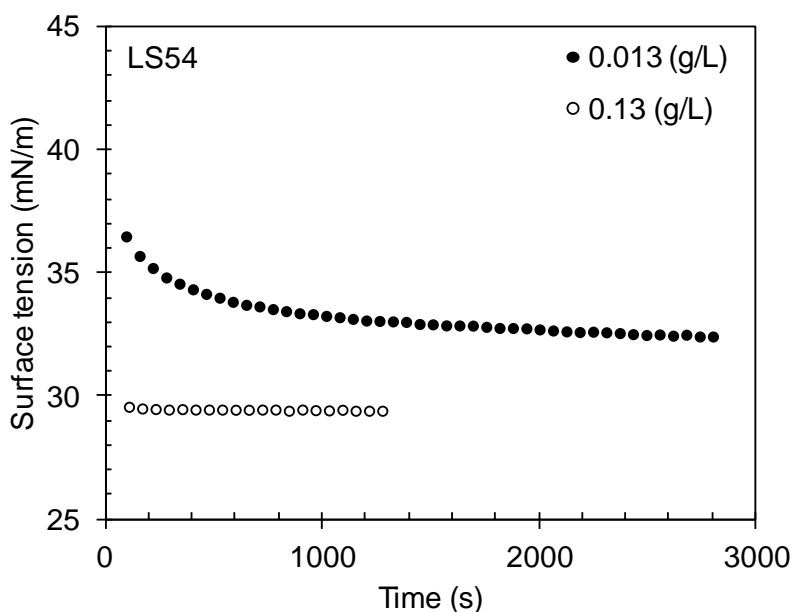
Fig. 3-5 Graph showing surface tension (mN/m) of 0.13 and 0.013 g/L LS54 solution against time (seconds) by Wilhelmy plate method.

3.3   Results and discussion

Both for the simplified drop weight method and the Wilhelmy plate method, a graph of surface tension versus log of concentration was used to determine the cmc point.[21] Fig. 3-6 (a) and (b) show the surface tension for solutions of LS45 and LS54 measured by Wilhelmy plate method. As the surfactant was added to ultrapure water and its concentration in the solution became higher, the surface tension of the ultrapure water gradually decreased to a

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[21] Rogerson.

minimum and levelled off. The graphs of g/L concentration against surface tension yield two straight lines with an intercept at the cmc.[22] The resulting cmc of LS45 and LS54 was 0.015 g/L and 0.0055 g/L, respectively.

Fig. 3-7 (a) and (b) give the surface tension for solutions of LS45 and LS54 measured by the simplified drop weight method. In these results, three straight lines could be depicted for determination of apparent cmc. It might be argued that these two yield points around cmc refer to pre- and post-micellar regions of surfactant.[23] However, further testing is needed to observe these regions and this argument is beyond this research aim. The apparent cmc value of LS45 and LS54 was 0.55-0.9 g/L and 0.4-0.59 g/L, respectively. Unlike the Wilhelmy plate method, this simplified drop method is utilized for dynamic surface tension. It is known that the cmc values obtained from dynamic surface tension measurements tend to be higher than static surface tension measurements,[24] and hence the cmc value of simplified drop weight method is higher around 100 times than that of Wilhelmy plate method. However, as the simplified drop weight method is not an accurate surface tension measurement, the value of it should be considered as an indicative cmc value.

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[22] Interpretation of data was generously advised by Prof. Kawase at the Kyoto Institute of Technology. He has researched on surface physical chemistry since 1973 and published numerous papers about surfactants, detergency and surface modification of fibres. Rather than conducting curve fitting with Microsoft Excel, it was recommended to see the data points as a whole by a logarithmic scale and determine linear curves.

[23] R. De Lisi, S. Milioto, and N. Muratore, "Thermodynamic Evidence of Cyclodextrin−Micelle Interactions," *The Journal of Physical Chemistry B* 106, no. 35 (Spring 2002): 8944, doi:10.1021/jp013648m.

[24] Cutler and Davis, *Detergency*, 627–632.
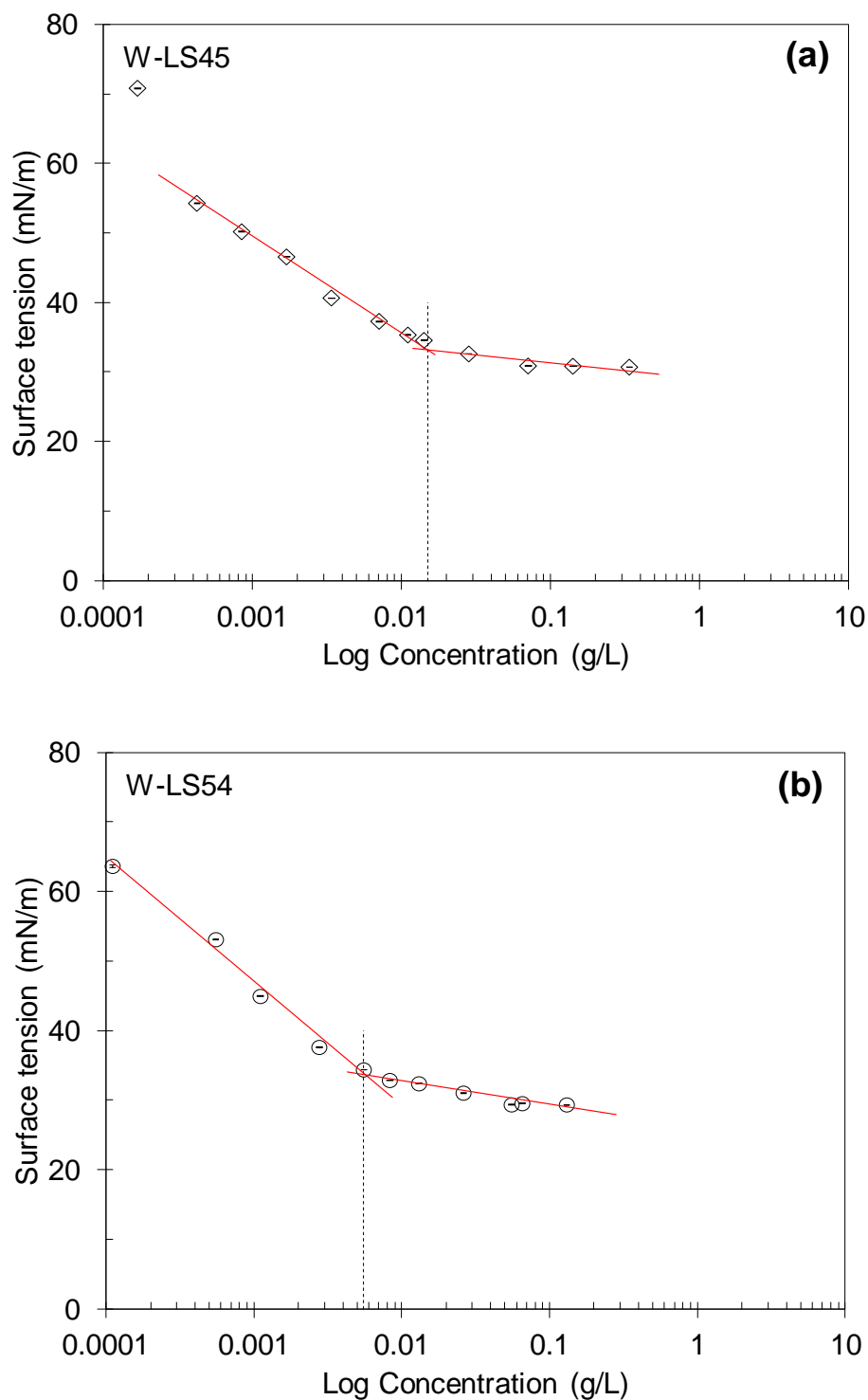
Fig. 3-6 Relationship between surface tension and concentration for LS45 (a) and LS54 (b) measured by Wilhelmy plate method.
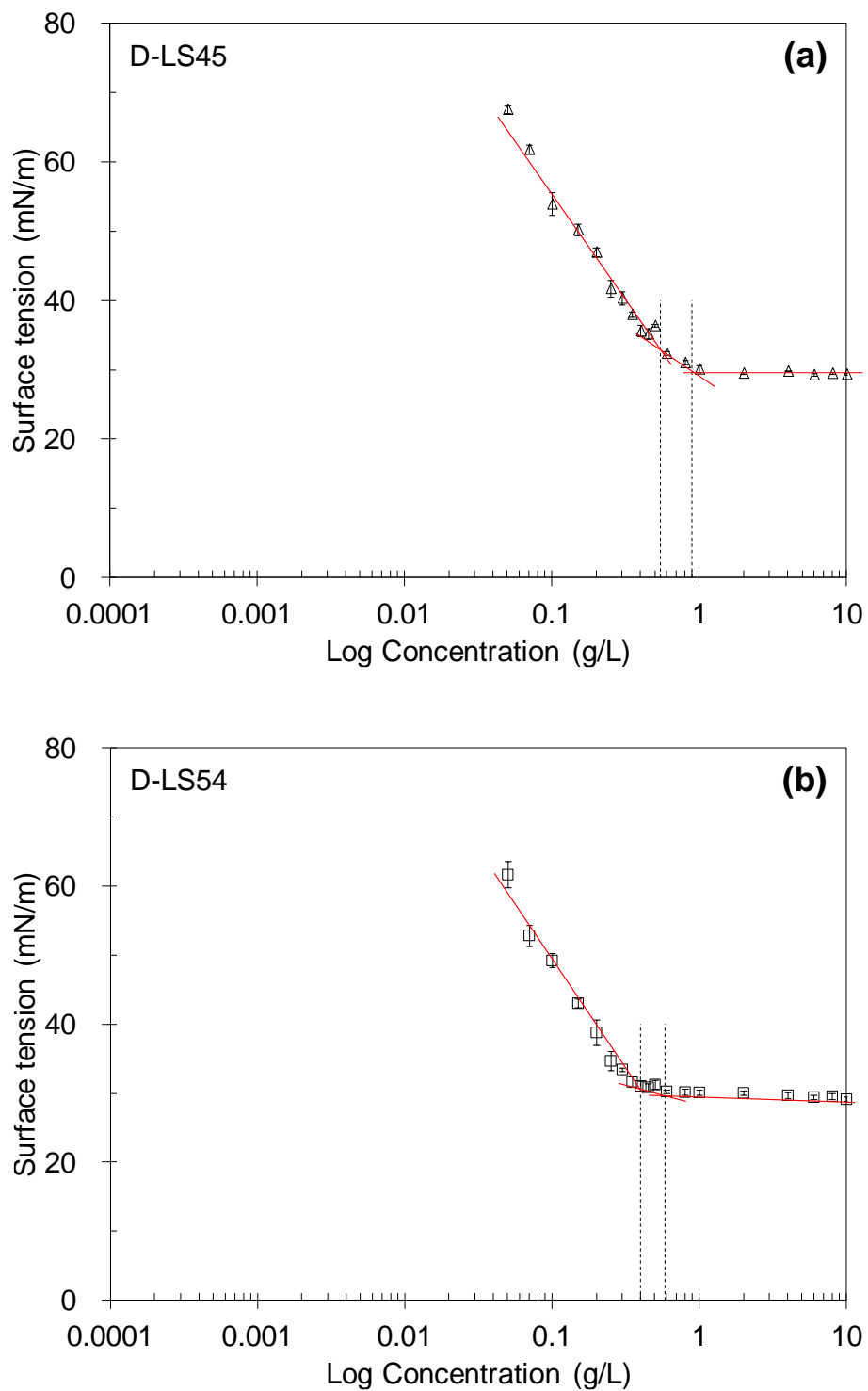
Fig. 3-7 Relationship between surface tension and concentration for LS45 (a) and LS54 (b) measured by simplified drop weight method.

Table 3-1 The cmc values (g/L) of LS45 and LS54 reported in previous research and this experiment.

	Previous research		This experiment	
	Sugden's bubble[25] (Dynamic)	Du Noüy ring, used by BASF (Static)	Simplified drop (Dynamic)	Wilhelmy plate (Static)
LS45	0.598	0.015 [26]	0.55 - 0.9	0.015
LS54	N/A	0.010	0.4 - 0.59	0.006

The cmc values of LS45 and LS54 reported in previous research and measured in this research are summarised in Table 3-1. It can be clearly seen that by measuring cmc values by the Whilhelmy plate method, the value for LS45 was exactly same and that of LS54 similar to BASF's cmc value measured by Du Noüy ring method, as they are both measuring static surface tension. In contrast, the range of the apparent cmc value of LS 45 determined by simplified drop method was corresponded to the cmc by Sugdens's bubble method. As interfacial phenomenon of surfactants during wet cleaning is similar with the state of dynamic surface tension,[27] cmc of LS54 by simplified drop method, 0.4-0.59 g/L can be considered as a reference or indicative cmc value for wet cleaning at the moment. However, further accurate measurement by dynamic surface tension method is needed to gain the exact cmc value. It would be possible to work out a correction factor for the simplified method calculation.

From the literature and experimental cmc value of LS45 and LS54, it was found that LS45 has higher cmc than LS54 in both dynamic and static surface tension measurement. In general, a surfactant that has higher cmc tends to have a higher cloud point, more hydrophilic character and longer alkyl chain than a surfactant having a lower cmc.[28,29] Although LS54

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[25] Sugden bubble method conducted by Field et al. in 2004.

[26] Schwarze et al., "Rhodium Catalyzed Hydrogenation Reactions in Aqueous Micellar Systems as Green Solvents," 475–477.

[27] Tikazawa and Tajima, *Basic Chemistry Course: Surface Chemistry*, 24.

[28] Matthew A. Cowell et al., "Partitioning of Ethoxylated Nonionic Surfactants in Water/NAPL Systems: Effects of Surfactant and NAPL Properties," *Environmental Science & Technology* 34, no. 8 (Spring 2000): 1587, doi:10.1021/es9908826.

[29] Tianhong Zhang and Roger E. Marchant, "Novel Polysaccharide Surfactants: The Effect of Hydrophobic and Hydrophilic Chain Length on Surface Active Properties," *Journal of Colloid and*

has higher cloud point and is more hydrophilic due to lower number of PO (propylene oxide) as given in Table 1, cmc of LS54 is lower than LS45. This might be explained that LS45 has longer alkyl chain than LS54 while further research is needed to confirm this point. This was investigated further by infrared spectroscopy, as discussed in Chapter 5.

3.4   Conclusion

To determine cmc value of Dehypon® LS45 and LS54, static surface tension was measured by Wilhelmy plate method and dynamic surface tension was obtained by simplified drop weight method. The salient features of this chapter can be summarized as follows:

1. The apparent cmc value of LS54 determined by dynamic surface tension ranged from 0.4 to 0.59 g/L. This value could help with deciding concentration of LS54 solution for wet cleaning by giving an indicative value for cmc. The advantage of this method would be more realistic and applicable method for textile conservators, while limitation can be depicted for determination of apparent cmc.

2. Through the experiments, the cmc values of LS54 were found to be lower than that of LS45. This can reduce the amount of detergent for wet cleaning and has benefits for reducing the environmental impact of its use in conservation as well.

3. Although LS54 has higher cloud point and is more hydrophilic due to lower number of PO (propylene oxide), its cmc is lower than LS45. This might be because the length of alkyl chain of LS54 is shorter than LS45. This is discussed in Chapter 5.

Chapter 4

Evaluation of detergency

4.1   Introduction

The aim of the research described in this chapter was to find out the optimum condition for wet cleaning with Dehypon® LS54 in relation to Dehypon® LS45 based on different concentrations, soaking time and agitation control. Artificially soiled cotton and wool fabrics were washed and their detergency effect on the soils on both fabrics was evaluated by measuring the reflectance value of the samples using colorimetry and spectroscopy. The effects of treatment on fibre surface morphology were evaluated by scanning electron microscopy (SEM) observation.

4.2   Experimental

4.2.1   Materials

Pre-soiled plain-weave cotton and wool fabrics were purchased from Materials Research Products Ltd. - specifically cotton with carbon black and olive oil (EMPA[1]-101) and wool with carbon black and olive oil (EMPA-107). These fabrics were kept in a refrigerator at 10 °C in order to prevent mould growth. Cotton and wool were selected because these fabrics are frequently encountered by textile conservators. The thread counts of the cotton were 60 for warp $\times$ 64 for weft per 10 mm, and those of the wool were 30 for warp $\times$ 35 for weft per 10 mm.

Dehypon® LS45 was purchased from Conservation By Design Ltd. Dehypon® LS54 was supplied by BASF (Badische Anilin- und Soda-Fabrik) in Germany. The Ramer® sponge (polyvinyl alcohol sponge) was purchased from Boots UK Ltd.[2] Softened water and

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[1] EMPA stands for German acronym, *Eidgenössische Materialprüfungs- und Forschungsanstalt,* which means The Swiss Federal Laboratories for Materials Science and Technology.
[2] The chemical sponge was selected rather than natural sponges as its size and resilience are more

deionised water were used for washing and rinsing, respectively.

4.2.2   Sample preparation

Each soiled fabric was cut to an 80×80 mm square, which allowed sufficient area needed for colour measurements. Each sample was numbered with a graphite 4B pencil, which would not interfere with the results and would not be removed in the wash bath, on the reverse side of the side to be tested.

4.2.3   Treatments

Four wet cleaning procedures, Experiments A, B, C and D, were designed for this research in order to evaluate the effects of lengthening conservation procedure, concentration, soaking time and the number of times of sponging on the efficiency of wet cleaning. The details were described as below and summarised in Table 4-1. Throughout the experiments, the soiled fabrics were washed only on the side where the sample number was not written. As a control group, the soiled fabrics were washed in softened water without surfactant. All experiments were carried out at room temperature (23-24 °C and 36-53%RH), while the wash solution of Dehypon® LS45 was cooled in a refrigerator overnight at 10 °C and then it was immediately used around 10 °C at room temperature. Each concentration of solution (weight /volume %) was prepared using an electronic balance and a measuring cylinder. For instance, to prepare 0.3% w/v LS45 solution, 0.3 g LS45 was dissolved in 1 litre of softened water.

consistent.

Table 4-1 The summary of experimental design and test variables.

	Experiment	Fibre	Surfactant	Concentration (% w/v)	Washing time (min)			Sponging (times)
					Soak	Wash	Rinse	
A	Conservation	Cotton Wool	LS45	0, 0.0075, 0.06, 0.18, 0.3	8*	20*	22*	60*
			LS54	0, 0.005, 0.004, 0.12, 0.2, 0.3				
B	Concentration	Cotton Wool	LS45 LS54	0, 0.06, 0.08, 0.1, 0.3, 0.5	N/A	5	2	100
C	Soaking time	Cotton Wool	LS54	0.3	5, 20, 40, 60	5	2	10
D	Sponging times	Wool	LS54	0.06, 0.3	N/A	5	2	50, 100, 150, 200, 300

- **Experiment A: Conservation Wet Cleaning**

Firstly, a standardized conservation wet cleaning procedure was set up, based on a number of previous wet cleaning research projects.[3,4,5] Table 4-2 shows the wet-cleaning procedure used for this research. The concentration of wash solution LS45 and LS54 was decided on the basis of their critical micelle concentration (cmc) provided by BASF, Fields et al.[6] and the tentative value according to V&A explained in Chapter 2, as well as the

Table 4-2 The wet cleaning procedure in Experiment A.

Dehypon®	Concentration (% w/v)				
	x5 cmc BASF*	x1 cmc	x3 cmc	x5 cmc	x7.5 cmc
LS45	0.0075	0.06	0.18	0.3	-
LS54	0.005	0.04	0.12	0.2	0.3

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[3] John A. Fields et al., "Finding Substitute Surfactants for Synperonic N," *Journal of the American Institute for Conservation* 43, no. 1 (2004): 55–73.

[4] Jane Lewis and Dinah Eastop, "Mixtures of Anionic and Non-ionic Surfactants for Wet‐cleaning Historic Textiles: A Preliminary Evaluation with Standard Soiled Wool and Cotton Test Fabrics," *The Conservator* 25, no. 1 (2001): 73–89, doi:10.1080/01410096.2001.9995166.

[5] Tarja H. Reponen, "The Effects of Conservation Wet Cleaning on Standard Soiled Wool Fabric: Some Experimental Work," ed. Janet Bridgland, vol. 1 (presented at the ICOM Committee for Conservation tenth triennial meeting, Washington, DC, 1993), 321–26, http://www.bcin.ca/Interface/openbcin.cgi?submit=submit&Chinkey=117116.

[6] Fields et al., "Finding Substitute Surfactants for Synperonic N."

experimental cmc value in chapter 3 (Table 4-3). The wet cleaning cycle was lengthened and repeated in order to more accurately replicate the common wet cleaning treatment for historical objects. Samples were pre-soaked in 500 ml of wash solution (concentration is given in Table 4-3) for two minutes and then washed by sponging each sample twenty times for five minutes in total. This process was repeated twice before changing into a second wash bath. After washing, the samples were then rinsed four times for five minutes in each with twenty times sponging each in softened water, and finally, they were immersed in deionised water for two minutes. Three specimens were prepared per test and six specimens (three cottons and three wools) were washed in the same bath to keep the testing consistent (Fig. 4-1). The samples were dried on the Melinex® sheet overnight.

Table 4-3 The concentration of Dehypon® LS45 and LS54 in Experiment A.

	Stage	Solution	Process	Time (min)
1	Wash	Surfactant (Soften water)	Soak	2
			Sponge (20 times)	5
			Soak	2
			Sponge (20 times)	5
	Change Solution			
2	Wash	Surfactant (Soften water)	Soak	2
			Sponge (20 times)	5
			Soak	2
			Sponge (20 times)	5
	Change Solution			
3	Rinse	Soften water	Sponge (20 times)	5
	Change Solution			
4	Rinse	Soften water	Sponge (20 times)	5
	Change Solution			
5	Rinse	Soften water	Sponge (20 times)	5
	Change Solution			
6	Rinse	Soften water	Sponge (20 times)	5
	Change Solution			
7	Rinse	Deionised water	Soak	2
	Change Solution			
			Total	50

Fig. 4-1 Conducting wet cleaning on soiled fabrics.

- **Experiment B: Concentration**

Following Experiment A, the effects of concentration, soaking time and the number of times of sponging were examined in Experiments B to D. The wet cleaning process was simplified to evaluate those effects clearly. In each test, only one specimen was tested because of time limitation.

In order to evaluate the effect of concentration on the removal of soiling, further washing tests were carried out by using a wide range of concentration (weight /volume %) at 0, 0.06, 0.08, 0.1, 0.3 and 0.5% w/v. The reason why this range of weight volume concentration was chosen in this experiment, rather than cmc, was in order to see the efficiency of wet cleaning based on the amount of surfactants. In addition, 0.5% w/v was selected because this is a higher concentration than $\times 5$ cmc in Experiment A for both LS45 and LS54. A sample was washed by sponging 100 times for five minutes. After washing, the

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sample was immersed in softened water and changed four times every two minutes. Then, the sample was dried on the Melinex® sheet overnight.

- **Experiment C: Soaking Time**

The washing effect of soaking time on removing soil on cotton and wool was determined by changing pre-soaked time before sponging. A sample was pre-soaked in 200 ml of wash solution for three different time periods of five, twenty, forty and sixty minutes and then washed by sponging ten times for each sample (Fig. 4-2). The rinsing process was the same as Experiment B.
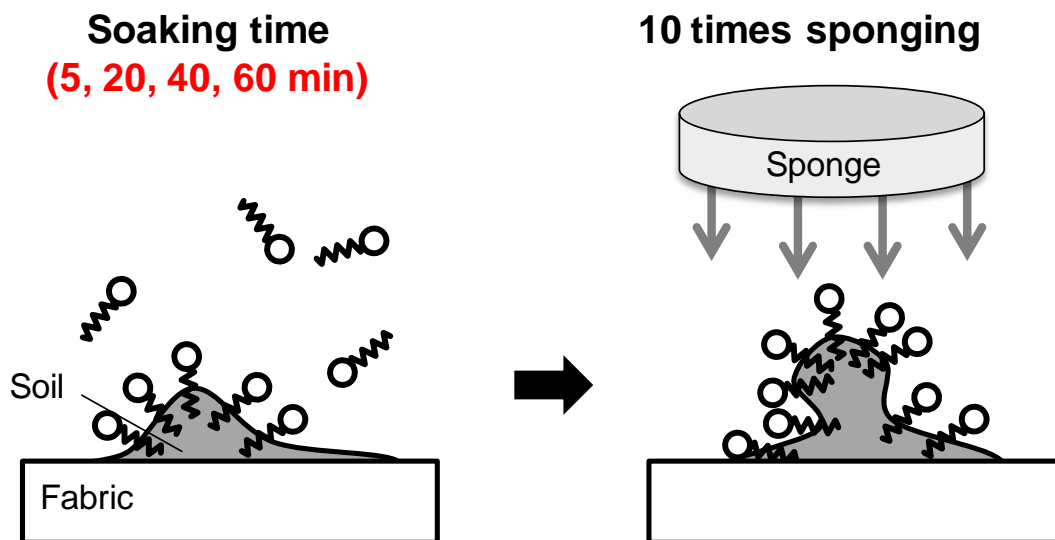
Fig. 4-2 A hypothesised model of soil release in Experiment C for evaluation of soaking time.

- **Experiment D: The Number of Times of Sponging**

The aim of Experiment D was to evaluate the effect of agitation on removal of soil on wool by changing the number of times of sponging. A sample was washed by different sponging times of zero, 50, 100, 150, 200 and 300 for five minutes. The rinsing process was the same as Experiment B.

4.2.4 Measurement

- **Colour measurement**

Soil removal was determined instrumentally by recording reflectance values on the soiled samples before and after washing using a Konica Minolta CM-2600d spectrophotometer (8 mm aperture, 10° viewing angle, D65/SCI illumination).[7] As the weave structure of wool was low density and slightly opened, the test samples were piled up and/or folded into six layers for readings in order to avoid picking up background readings caused by the open weave. Three measurements were carried out on one specific position for each soiled fabric (Fig. 4-3).

The reflectance reading R of each soiled fabric, which represents greyness, was obtained in a range from 360 to 740 nm wavelength at 10 nm intervals. This R value can be used for the Kubelka-Munk theory to determine a quantity of appearance soil content, which is relating reflectance and absorption of light from the spectrophotometer, and have been widely used in detergency studies.[8,9,10] According to the Kubelka-Munk theory, K/S (K is the absorbance coefficient, and S is the scatter coefficient) is calculated by the Equation 1 and directly proportional to the colour strength (content) of a soiled fabric.[11,12]

$$K/S = (1\text{-R})^2/2\text{R} \qquad \text{Equation 1}$$

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[7] The measurement was conducted at the Kyoto Institute of Technology, Japan.

[8] John Oakes and Sarah Dixon, "Adsorption of Dyes to Cotton and Inhibition by Surfactants, Polymers and Surfactant–polymer Mixtures," *Coloration Technology* 119, no. 6 (Spring 2003): 317, doi:10.1111/j.1478-4408.2003.tb00190.x.

[9] Keiko Gotoh, "Investigation of Optimum Liquid for Textile Washing Using Artificially Soiled Fabrics," *Textile Research Journal* 80, no. 6 (April 1, 2010): 3, doi:10.1177/0040517509340605.

[10] Ruben Mercade-Prieto and Serafim Bakalis, "Methodological Study on the Removal of Solid Oil and Fat Stains from Cotton Fabrics Using Abrasion," *Textile Research Journal*, June 13, 2013, 55, doi:10.1177/0040517513490059.

[11] L. Loeb, P. B. Sanford, and S. D. Cochran, "Soil Removal as a Rate Process," *Journal of the American Oil Chemists' Society* 41, no. 2 (February 1, 1964): 120–24, doi:10.1007/BF02673487.

[12] Nicholas Eastaugh, "Some Experiments Comparing the Performance of Detergent Formulations Based on Anionic and Non-Ionic Surfactants under Conditions Relating to Conservation Use," ed. Kirsten Grimstad, vol. 1 (presented at the ICOM committee for conservation: 8th triennial meeting, Sydney, Australia: Getty Conservation Institute, 1987), 357–64.

Fig.4-3 Measuring the reflectance value of soiled fabric by spectrophotometer at the KIT.

The wavelengths from 400 nm to 700 nm are in the visible light region. By choosing a single measurement wavelength in this region and measuring differences in the test samples, colour changes visible to the eye can be determined. For detergency studies in textile conservation, in order to evaluate detergency by way of using a spectrophotometer, Eastaugh[13] selected the wavelength at 460 nm, Shashoua[14] selected 500 nm and Jane selected 560 nm.[15] In this research, 560 nm was selected as the spectrum becomes constant from 460 nm, and 560 nm is the maximum sensitivity to human eyes under light condition because of the Purkinje effect.[16]

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[13] Nicholas Eastaugh, vol. 1.

[14] Yvonne Shashoua, "Investigation into the Effects of Cleaning Natural, Woven Textiles by Aqueous Immersion," ed. Kirsten Grimstad (presented at the ICOM Committee for Conservation, 9th triennial meeting, Dresden, German Democratic Republic, 1990), 313–18, http://www.bcin.ca/Interface/openbcin.cgi?submit=submit&Chinkey=107271.

[15] Jane Wild, "Experimental Work Comparing the Performance of Wash Bath Additives Used in the Aqueous Immersion Cleaning of a Series of Standard Soiled Fabrics" (presented at the AICCM Textiles Symposium 2006, Adelaide, Australia, 2006), 19–30, http://www.aiccm.org.au/aiccm-publications/conference-proceedings/experimental-work-comparing-performance-wash-bath.

[16] Hugh Davson, *Physiology of the Eye* (Elsevier, 2012), 329.

Using values of *K/S* at 560 nm for unsoiled and soiled fabric, relative percent detergency (%) was calculated (details are explained in section 4.3) and the efficiency of wet cleaning was evaluated.

The L*a*b* value of soiled fabrics was also measured before and after washing according to the CIELAB system. This assessment method has been more common in textile conservation and the data was considered helpful for comparison with previous research. The +a*/-a* axis represents colours from magenta to green, while the + b*/-b* axis represents those from yellow to blue. The expression L* represents lightness; it has values from 0 (black) to 100 (white).[17] Therefore in this research, the L*value was used to evaluate the colour change of solid fabrics. However, it should be understood that the colour difference (∠E) of soiled fabric often does not correlate with the degree of soil removal.[18] The reason why it is still used could be to monitor for another effect, such as the build-up of coloured residues.

• **Microscopic observation**

Microscopic observation of the fabric surface can help evaluate whether any particulate soiling was reduced or any residues had been deposited or if fibres had been damaged such as abrasion after wet cleaning. Observation of the fabric surface before and after wet cleaning was undertaken using an optical digital microscope (KEYENCE VHX-900) (Fig. 4-4).[19] The fibre surface was studied using a Hitachi S-4200 Field Emission Scanning Electron Microscope (FE-SEM). All the fibres were gold coated using ion sputtering equipment (JEOL Ltd., JFC-1100E) at 6 mA for four minutes prior to the FE-SEM measurement.[20]

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[17] Ágnes Timár-Balázsy, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann Series in Conservation and Museology (Oxford: Butterworth-Heinemann, 1998), 86–87.
[18] Ágnes Tímár Balázsy, "Wet Cleaning of Historical Textiles: Surfactants and Other Wash Bath Additives," *Reviews in Conservation* 1 (2000): 57.
[19] The microscopic observation was conducted at the Kyoto Institute of Technology, Japan.
[20] The SEM observation was supported by Ph. D Candidate Mr. Keisuke Maeda at the Kyoto Institute of Technology, Japan.
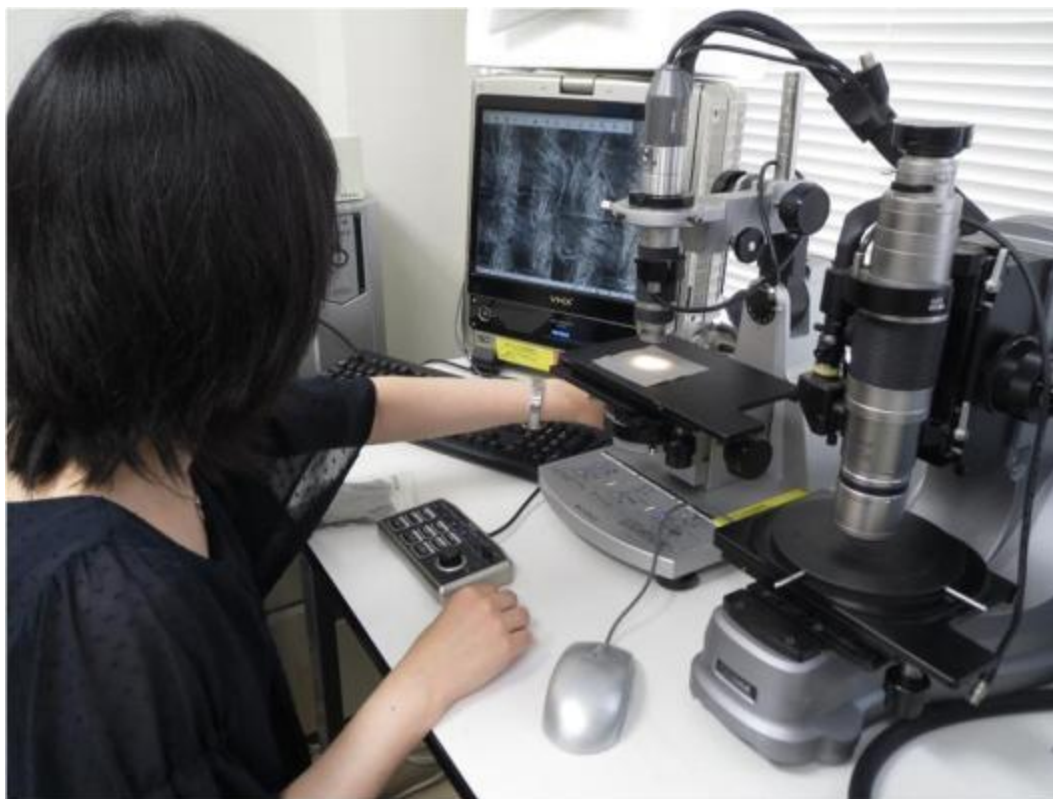
Fig. 4-4 Observing the surface of soiled fabric by an optical digital microscope at the KIT.

4.3 Results and discussion

4.3.1 Experiment A: Conservation Wet Cleaning

The samples were washed by LS45 and LS54 with a wide range of concentration from 0.005 to 0.3 % w/v, based on the experimental cmc of LS45 and LS54 explained in Chapter 3 (Fig. 4-5). With visual observation, both cotton and wool samples treated with LS45 and LS54 at 0.3% w/v significantly became lighter. Figs. 4-6 and 4-7 show surface of cotton and wool before and after washing with LS54 at 0.04 % w/v and 0.3 % w/v, observed under the microscope. It can be seen that the amount of black carbon on the surface of fabrics gradually reduced when the concentration of surfactants increased from 0 to 0.3% w/v.

Fig. 4-8 shows the L* value of samples treated in Experiment A. The L* of cotton washed by LS45 and LS54 has not been significantly changed from low to high concentration. In contrast, the L* of wool washed by LS45 and LS54 at 0.3% w/v has been increased compared with untreated samples.
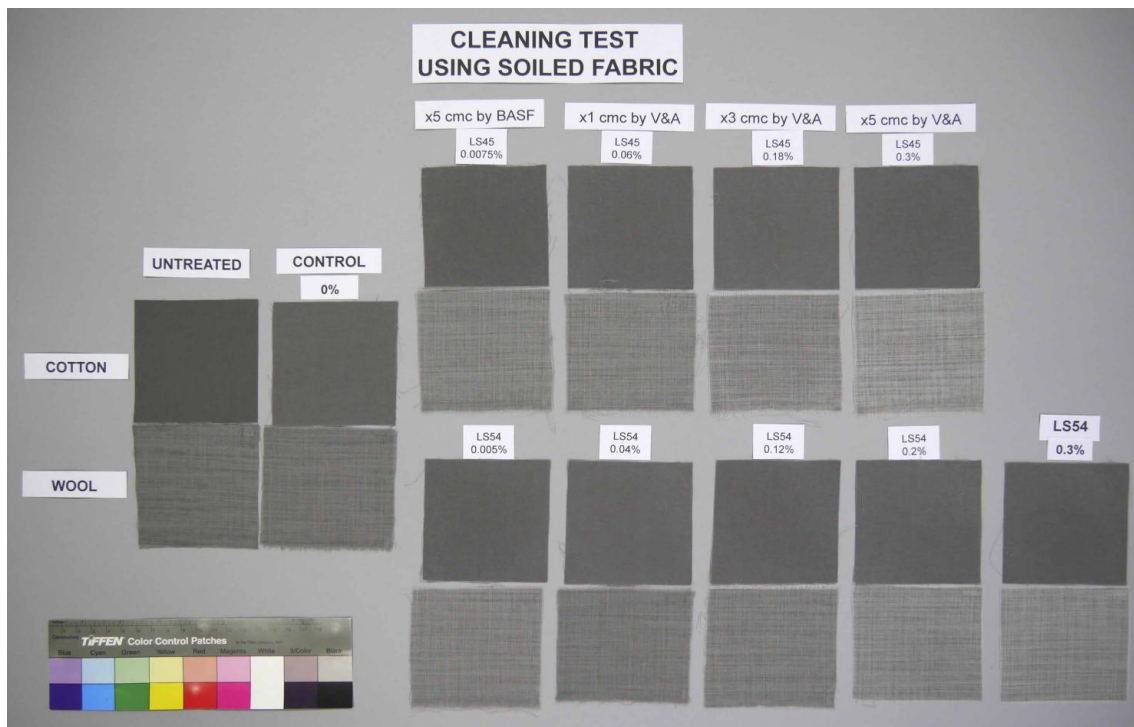
Fig. 4-5 Overview of the washed samples in Experiment A.
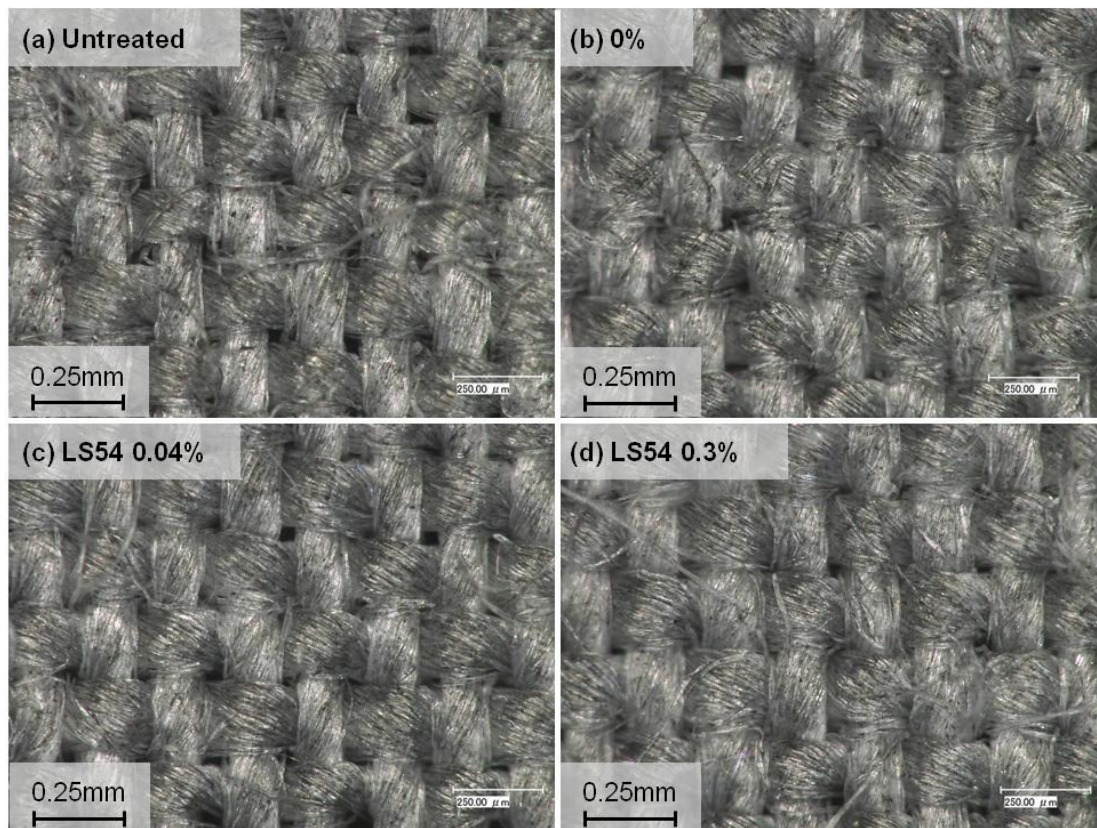
Fig. 4-6 Microscopic photographs of soiled cotton before (a) and after treatment with soften water (b), 0.04% w/v LS54 (c) and 0.3% w/v LS54 (d) in Experiment A.
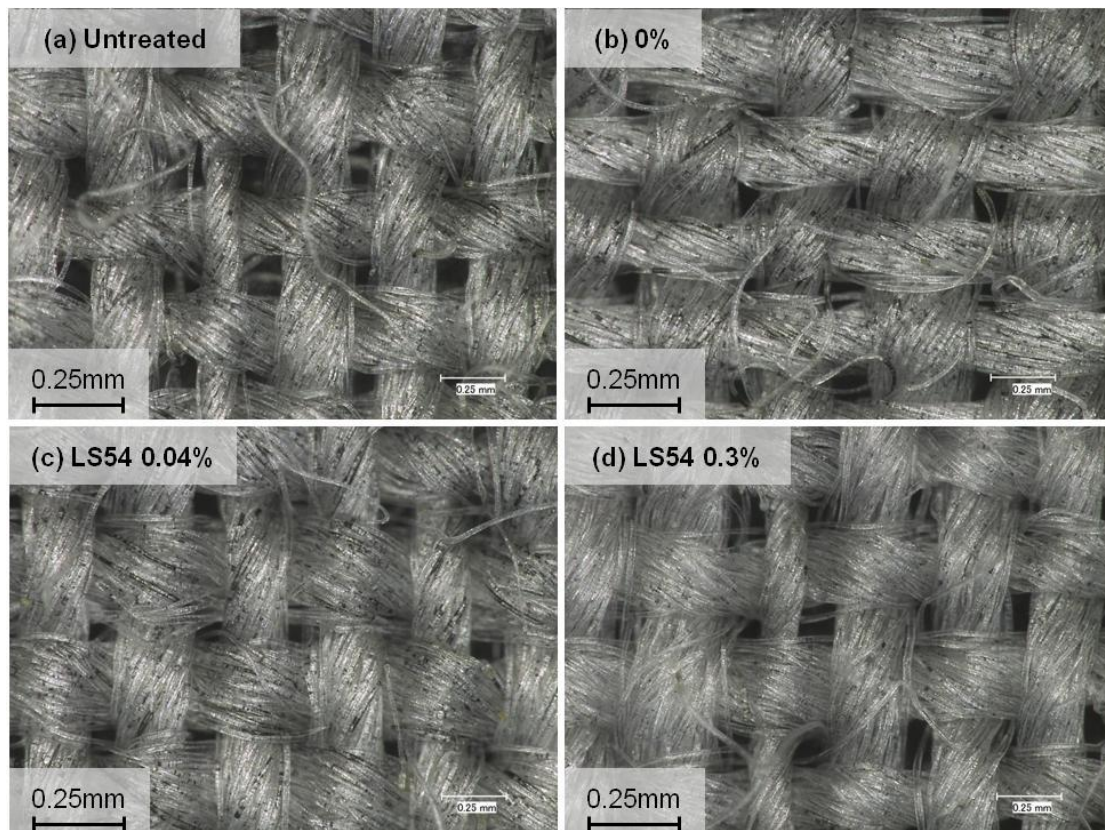
Fig. 4-7 Microscopic photographs of soiled wool before (a) and after treatment with soften water (b), 0.04% w/v LS54 (c) and 0.3% w/v LS54 (d) in Experiment A.
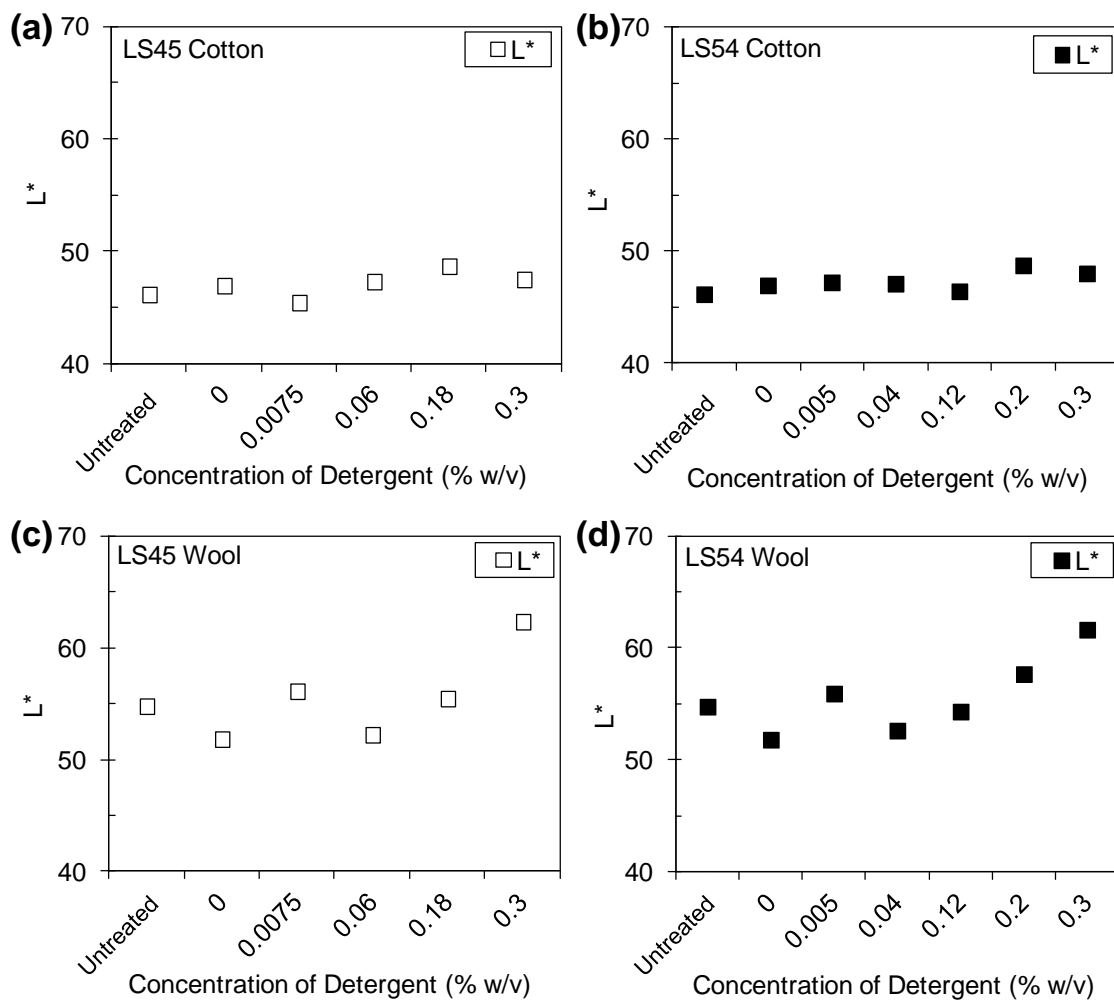
Fig. 4-8 Concentration-dependence of L* values showing before and after treatment: cotton washed by LS45 (a) and LS54 (b); wool washed by LS45 (c) and LS54 (d).

The *K/S* spectra of cotton and wool washed by LS45 and LS54 are given in Figs. 4-9 and 4-10. From each spectrum, *K/S* values at 560 nm were plotted versus the concentration of treatments (Figs. 4-9 and 4-10). The lower *K/S* value means that the reflectance of fabric becomes higher, indicating that the fabric is whiter and that the relative detergency effect on the soiled fabric has increased. The *K/S* of cotton and wool, which was washed by LS45 and LS54, decreased with the increasing concentration compared to no detergent in the treatment. In order to compare the efficiency of wet cleaning in every experiment, the changing rate of *K/S* after treatments; relative detergency (%), was calculated by the following Equation 2.

This is a relative value to compare the detergency of different concentrations of the different surfactants, especially for evaluating the efficiency difference between LS45 and LS54. The detergency is plotted against the concentration in Fig. 4-11. In this research, the soiled fabrics washed in softened water without surfactant were considered as a control.

$$\text{Detergency (\%)} = \frac{K/S_0 - K/S_t}{K/S_0} \times 100 \qquad \text{Equation 2}$$

K/S_0: Soiled fabric washed without surfactant, K/S_t: Soiled fabric washed with surfactant
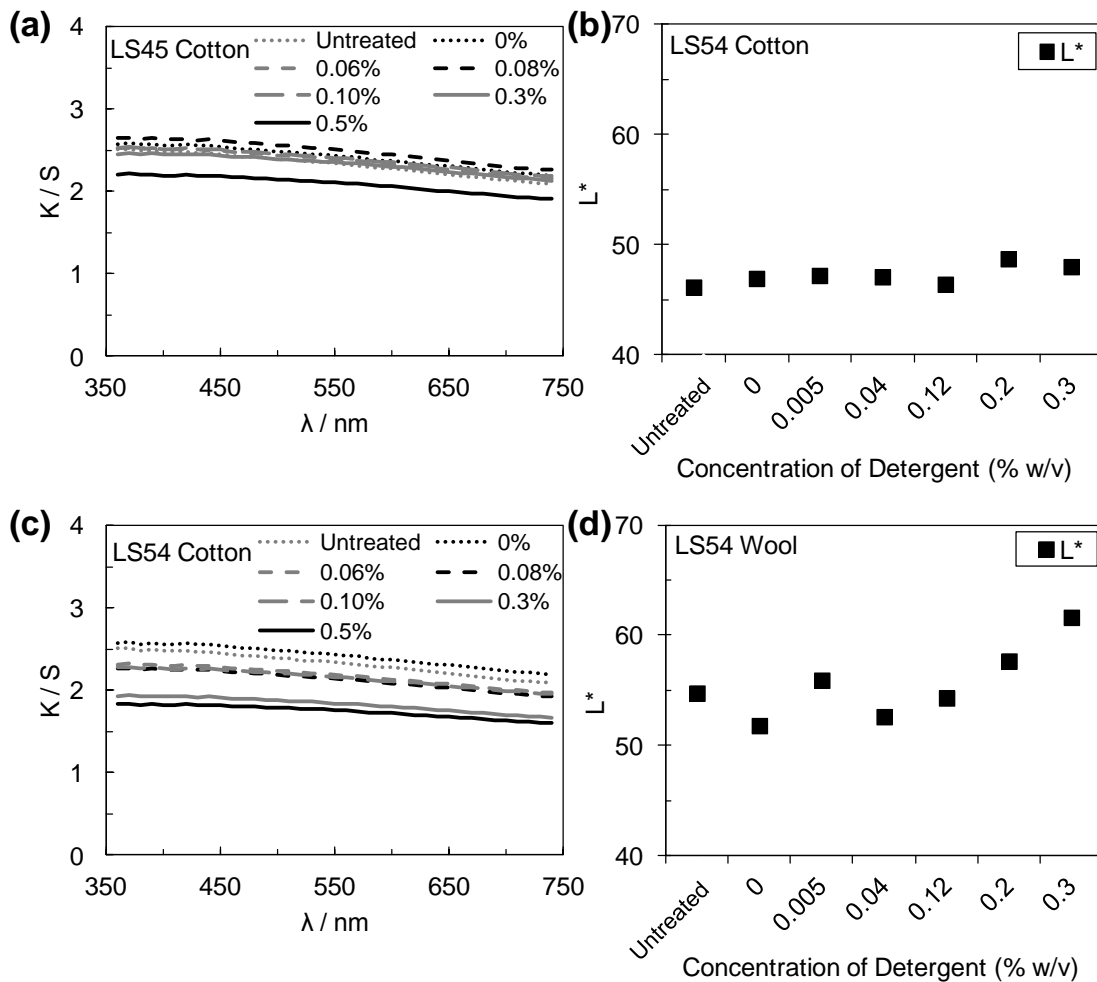
Fig. 4-9 The K/S spectrum (left) and concentration-dependence of K/S at 560 nm (right) of cotton washed by LS45 (a) (b) and LS54 (c) (d).
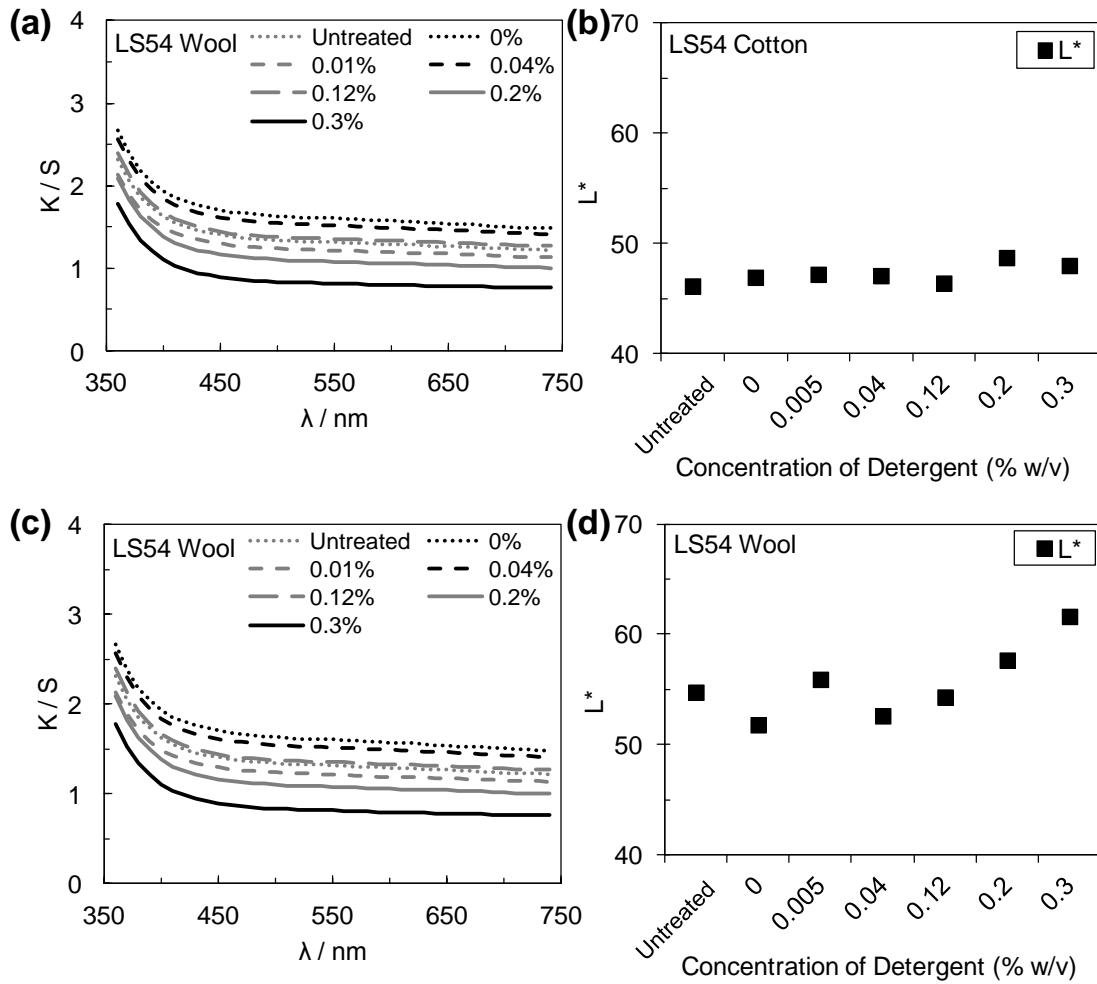
Fig.4-10 The *K/S* spectrum (left) and concentration-dependence of *K/S* at 560 nm (right) of wool washed by LS45 (a) (b) and LS54 (c) (d).
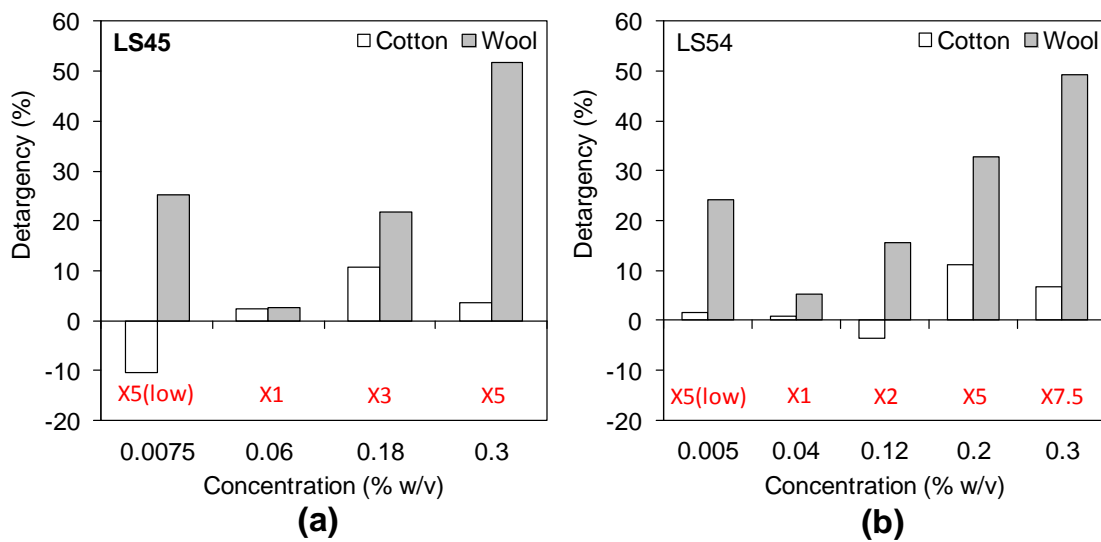
Fig. 4-11 Concentration-dependence of detergency for soiled cotton and wool fabrics washed by LS45 (a) and LS54 (b) in Experiment A.

There was no significant change in the detergency of cotton washed with LS45 and LS54, whereas both LS45 and LS54 at 0.3% w/v have the greatest effect of removing soil on wool, showing approximately 50% of detergency. As LS54 at 0.3% w/v is equal to $\times 7.5$ cmc, it was found that LS54 requires slightly higher cmc for washing in order to achieve the same effect of detergency as LS45.

Fig. 4-12 shows SEM micrographs of the surface morphology of the wool before and after washing with LS54 at 0, 0.04 and 0.3 % w/v. Compared to the untreated (before treatment) sample (Fig. 4-12 (a)), the amount of soil on the surface of control sample (washed in softened water, i.e. 0% w/v) was reduced (Fig. 4-12 (b)). After washing with LS54 both at 0.04 and 0.3% w/v (Figs. 4-12 (c) and (d)), the amount of particulate soiling was almost removed. It was found that the particulate soiling can be removed more effectively by washing with sponging and with surfactant at low concentration rather than by sponging with no detergent. In addition, there was no abrasion on the surface of fabric after treatment.
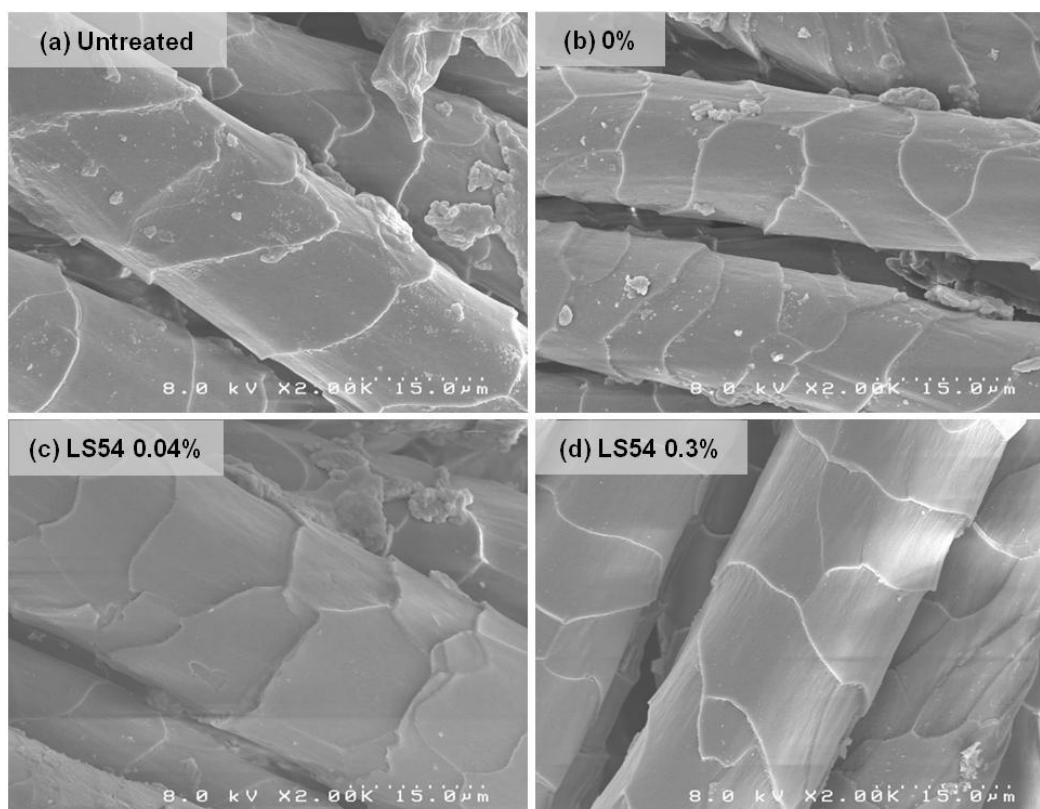
Fig. 4-12 SEM micrographs of wool surface before (a) and after washed by soften water (b) and LS54 at 0.04% w/v (c) and at 0.3% w/v (d).

The graphs showing L*a*b* and *K/S* values in Experiment A-D are to be found in Appendix 3

4.3.2   Experiment B: Concentration

Experiment B aimed to evaluate the effect of LS45 and LS54 concentrations on the removal of soiling by using a wide range of concentration from 0-0.5% w/v. In this experiment, consistent weight volume concentration was chosen rather than cmc in order to see the efficiency of wet cleaning based on the amount of surfactants. As the wet cleaning process was simplified compared with Experiment A, an initial test was carried out at 0 and 0.3% w/v and revealed the *K/S* values were almost the same as Experiment A (Fig. 4-13). Therefore, the shortened wet cleaning process in Experiment B, C and D would correspond approximately to Experiment A.
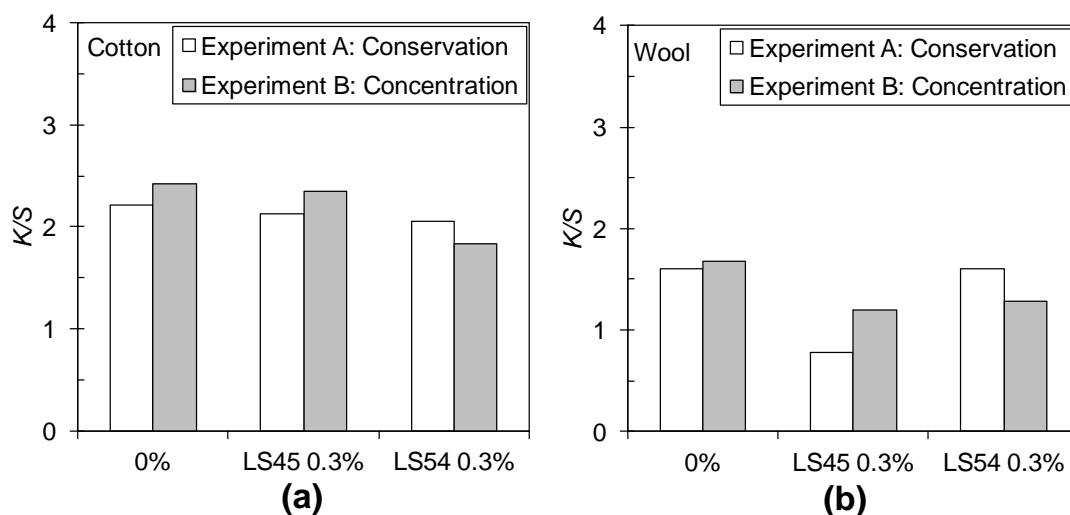
Fig. 4-13 The *K/S* value at 560 nm of cotton (a) and wool (b) washed by soften water, LS45 and LS54 at 0.3% w/v in Experiment A and B.

Fig. 4-14 gives an overall visual image of Experiment B. With visual observation, wool samples treated with LS45 and LS54 at 0.3 and 0.5% w/v significantly became lighter, whereas it was little hard to see the colour difference for cotton. Fig. 4-15 shows the efficiency of wet cleaning for cotton and wool washed by LS45 and LS54 plotted against concentration. As for cotton, the detergency of LS45 was constant from 0 to 0.5% w/v, while

that of LS54 increased by about 20% at 0.3 and 0.5 % w/v. In terms of wool, from 0.06 to

0.1 % w/v the detergency was not changed, whereas above 0.3% w/v the detergency of LS45

and LS54 increased at 30%, and at 0.5% w/v they reached 40% and 50%, respectively.

However from the aspect of practicality in conservation, 0.5% w/v of LS45 and LS54 was too

foamy to rinse effectively based on judgement criteria from common wet cleaning treatment

at the CTCTAH. Therefore, it is considered that 0.3% w/v of LS45 and LS54 was the optimal

concentration for washing.
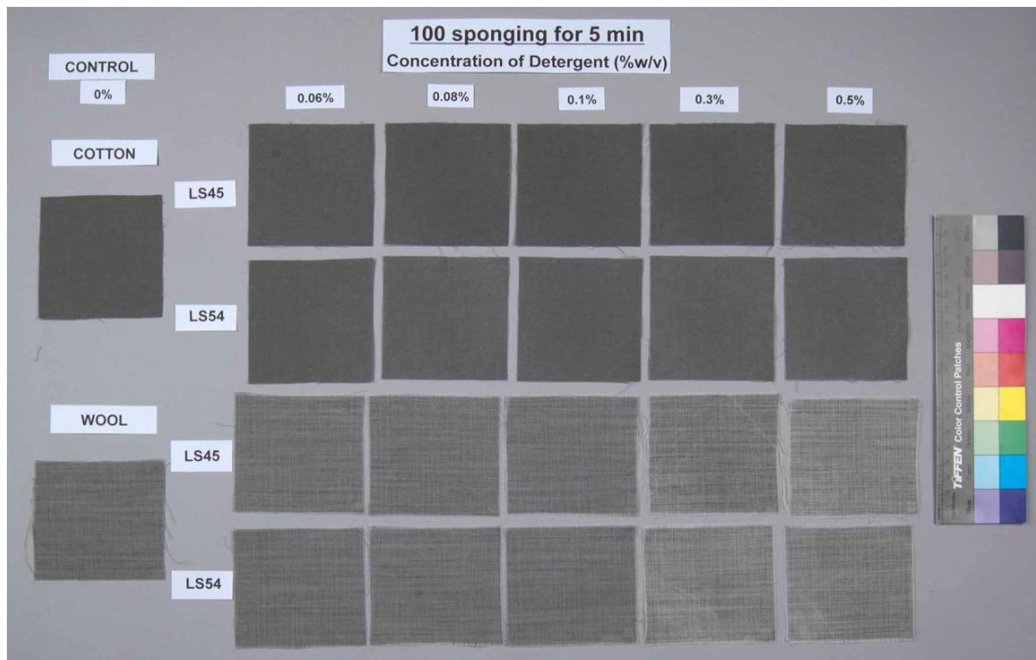
Fig. 4-14 Overview of the washed samples in Experiment B.
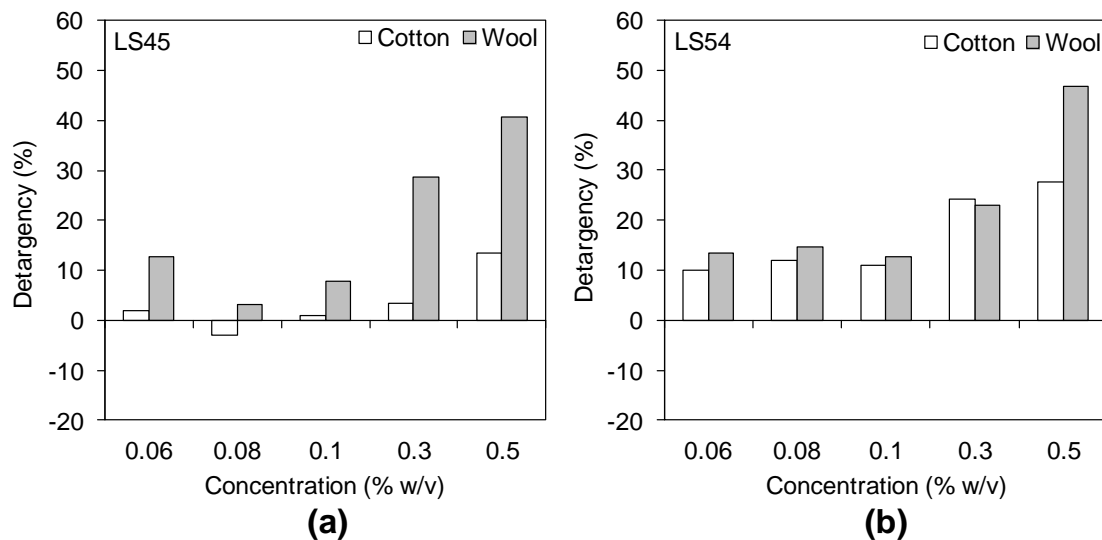
Fig. 4-15 Concentration-dependence of detergency for soiled cotton and wool fabrics washed by LS45 (a) and LS54 (b) in Experiment B.

4.3.3 Experiment C: Soaking Time

The effectiveness of detergency from soaking time was examined on cotton and wool using LS54 at 0.3 % w/v. With the naked eye, there was no change between five and sixty minutes (Fig. 4-16). Fig. 4-17 shows the results of detergency for soiled cotton and wool which is plotted against soaking time. It was found that there was no effect of removing soils from pre-soaking time for wet cleaning.
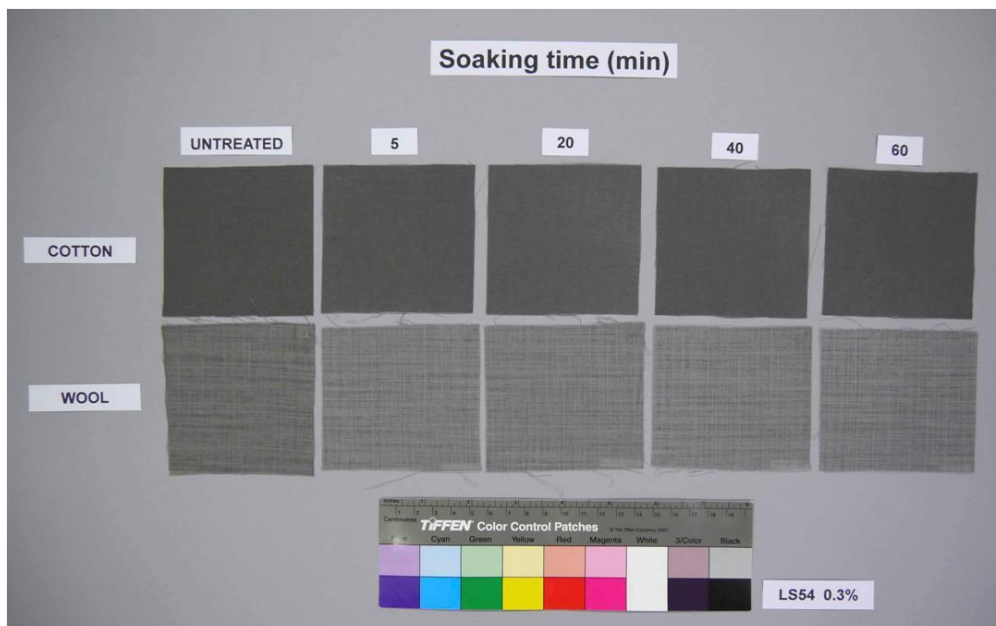
Fig. 4-16 Overview of the washed samples in Experiment C.
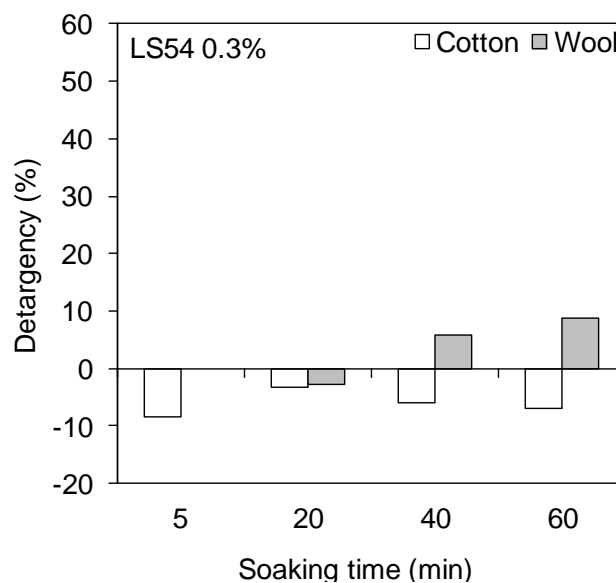
Fig. 4-17 Soaking time-dependence of detergency for soiled cotton and wool fabrics washed by LS54 at 0.3% w/v in Experiment C.

48

4.3.4   Experiment D: The Number of Times of Sponging

In Experiment A and B, the number of times of sponging was fixed at sixty (in total) and 100, respectively. In this experiment, the effect of agitation on removal of soil was examined by changing the number of times of sponging. The lowest concentration was at 0.06 % w/v and optimal concentration was at 0.3 % w/v of LS54, and this was obtained in Experiment B. By visual observation, 200 and 300 sponging at 0.3 % w/v visually made the fabric lighter in colour, i.e. became cleaner (Fig. 4-18). Under the microscope, the amount of soiling was significantly reduced from the surface of wool washed with 300 sponging at 0.3 % w/v, compared with zero sponging (Fig. 4-19). Fig. 4-20 shows the results of detergency for soiled cotton and wool which is plotted against the number of times of sponging. There was no apparent difference in detergency of wool treated at 0.06 % w/v throughout the experiment. In contrast, from 150 to 300 sponging with 0.3 % w/v LS54, the detergency of wool fabrics gradually increased to about 30% and 200 sponging showed the maximum detergency.
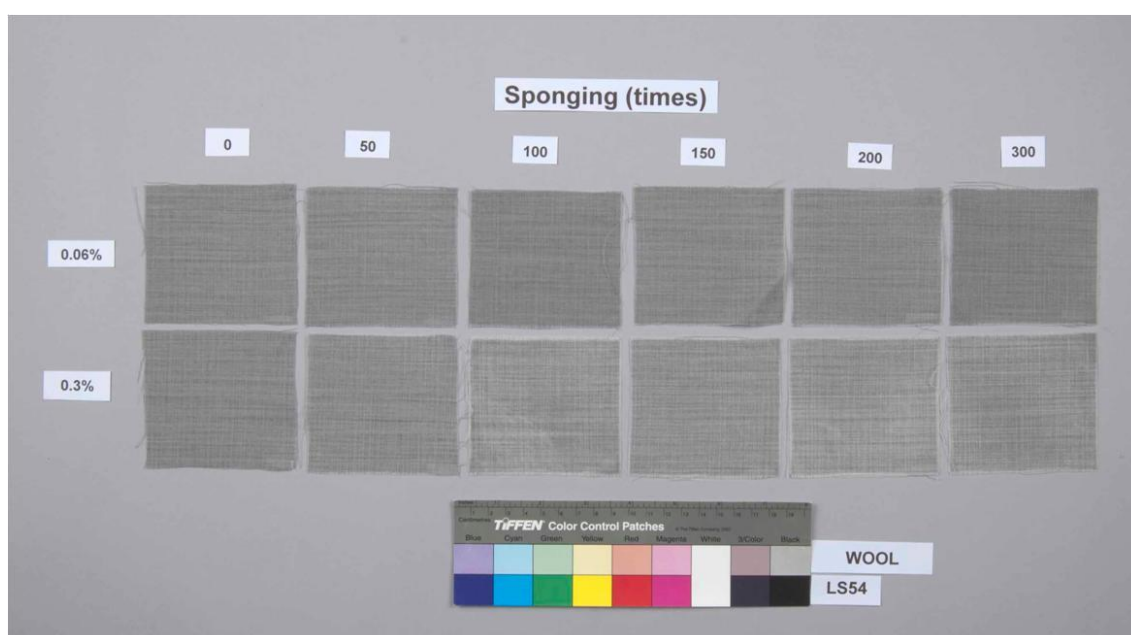
Fig. 4-18 Overview of the washed samples in Experiment D.
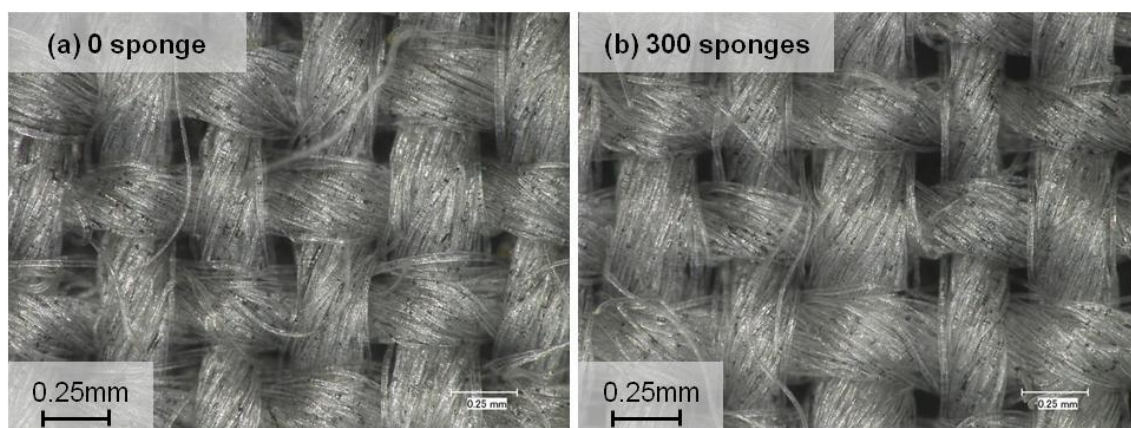
Fig. 4-19 Microscopic photographs of soiled wool washed by LS54 at 0.3% w/v without sponge (a) and with 300 sponging (b) in Experiment D.
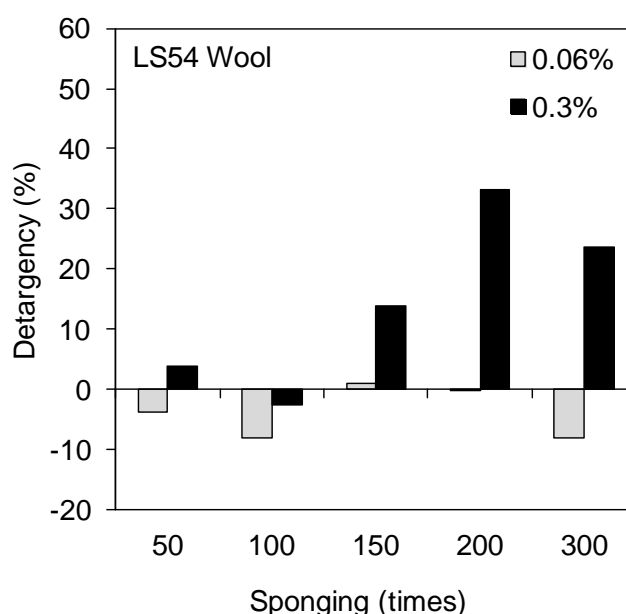
Fig. 4-20 Sponging times-dependence of detergency for soiled wool fabrics washed by LS54 at 0.06 and 0.3% w/v in Experiment D.

Fig. 4-21 shows SEM micrographs of the surface morphology of the wool before and after washing with zero and 300 sponging. Compared to the untreated and zero sponging wool (Figs. 4-21 (a) and (b)), the amount of particulate soils on the wool with 300 sponging was completely reduced (Fig. 4-21 (c)). Furthermore, there was no abrasion on the surface of fabric after 300 sponging, as observed by SEM in Fig. 4-21 (c).

Throughout the experiment, the higher number of spongings with optimal concentration of LS54 can enhance the detergency of wool. Although no physical damage can be seen on the surface of fabric, an excessive amount of sponging would not be

recommended as at over 200 sponging, treatment was of saturated detergency, and no more efficiency of soil removal would be observed. .
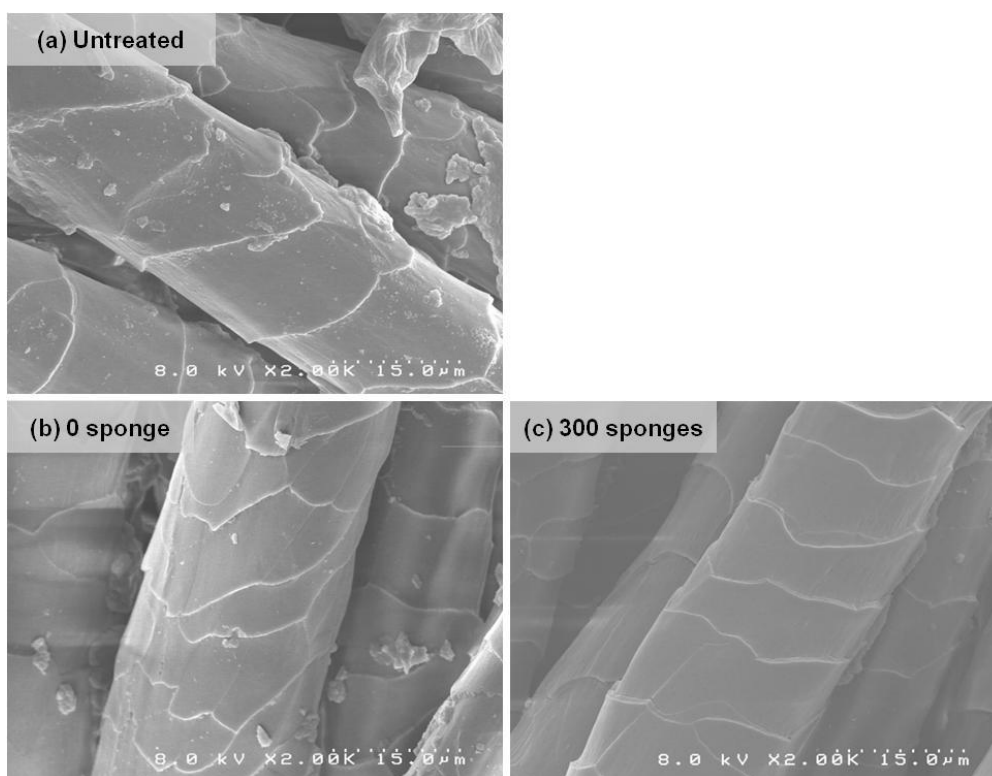
Fig. 4-21 SEM micrographs of wool surface before (a) and after washed by LS54 at 0.3% w/v without sponge (b) and with 300 sponging (c) in Experiment D.

4.4   Conclusion

To find out the optimum condition for wet cleaning with Dehypon® LS54, the detergency of soiled fabrics was examined by comparison with Dehypon® LS45. The results in this chapter suggest that the most effective concentration of LS54 for removing soils was 0.3 % w/v and its detergency effect was almost equal to LS45 at the same concentration. However, as LS54 at 0.3% w/v is equal to ×7.5 cmc, it was found that LS54 requires slightly higher cmc for washing in order to achieve the same effect of detergency as LS45. In contrast to LS45, however, it was observed that LS54 effectively worked for removing soils on cotton. It was also found that the longer pre-soaking time did not have a significant effect on the detergency of the soiled cotton and wool. In addition, the shortened washing time, but large amount of sponging, had similar detergency with the lengthened washing time but small

number of sponging. Thus, depending on the condition of textiles, it is important to select either total soaking time or sponging time and also the choice of appropriate concentration of LS54 to gain effective detergency and prevent further degradation of textiles.

Chapter 5

Analysis of residues on cotton and wool

5.1   Introduction

This chapter aims to develop an analytical method to determine whether Dehypon[®] LS45 (LS45) and Dehypon[®] LS54 (LS54) leave detectable residue on cotton and wool after washing and rinsing, and if they do, to identify any characteristic spectral differences relating to surfactant-fibre interaction. In this study, unsoiled cotton and wool were washed by LS45 and LS54, and with, or without, rinsing treatments the effects of residue on the chemical and physical properties of fibres were investigated by Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs), measurement of thickness of fabric and tensile test. The influence of wet cleaning on fibre surface morphology was evaluated by SEM (Scanning Electron Microscope) observation. LS45 and LS54 were also characterized by using DRIFTs with the aim of obtaining the characteristic spectral differences regarding the chemical structure.

As described in Chapter 2, some anionic surfactants show irreversible bonding, called chemisorb, onto proteinous fibres, such as wool and silk, caused by the chemical attraction between positive sites of the protein and negative charges of the surfactant.[1,2] Wet cleaning is a widely used conservation treatment for historical textiles; therefore using appropriate surfactants is vital for their long term preservation. Because wet cleaning is an irreversible treatment, conservators aim to minimize damage to objects during treatments. Therefore, it is vital to select appropriate surfactants to prevent the chemical interaction of the surfactant with textile fibres.

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[1] L. A. Holt and J. Onorato, "Substantivity of Various Anionic Surfactants Applied to Wool," *Textile Research Journal* 59, no. 11 (November 1, 1989): 653–57, doi:10.1177/004051758905901103.

[2] David E. Walker, "Surfactants in Textile Conservation," in *The Textile Speciality Group Postprints*, ed. P. Ewer and B. McLaughlin, vol. 5 (presented at the AIC's 23rd Annual Meeting, St Paul, Minnesota: The Textile Speciality Group of AIC, 1995), 29–34.

In the field of textile conservation, little research has been published about residues of surfactants on fibres, because it is analytically challenging and scientifically complex to detect very low concentrations of surfactant composing organic compounds on fabrics. Recent research were summarised in Chapter 2, while there is no established analysis for determination of residues of non-ionic surfactants on historical textiles. Therefore, it is considered that DRIFTs can help to address the issues of detecting low concentrations of surfactants on the woven fabric surfaces. The detail of DRIFTs technique and their application to the conservation field were described in Chapter 2.

5.2 Chemical Structure of Materials

Table 5-1 and Fig. 5-1 give the chemical and physical properties of cotton and wool, which were used for this research. Their molecular structures have an affinity for water because of many hydroxyl (–OH) and amide (–NH$_2$) groups in their chemical structures. Cotton and wool are therefore classed as hydrophilic (water-attracting) fibres, and they adsorb and desorb moisture with the surrounding air to maintain equilibrium between them. The ratio of crystalline to amorphous regions of fibre polymers also links closely to their moisture-absorbing properties, and determines their moisture regain. Water can penetrate the amorphous polymer regions more easily than the crystalline regions. Wool has more amorphous regions than cotton and therefore has a greater moisture regain and capacity for water absorption than cotton.[3,4,5]

The chemical structure of Dehypon® LS45 and LS54 is described in Chapter 2.

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[3] Foekje Boersma, *Unravelling Textiles: A Handbook for the Preservation Oftextile Collections* (London: Archetype, 2007), 3.

[4] Nobuko Naruse, *Basic Science of Clothing Material* (Tokyo: Bunka Publication, 2006), 22–25.

[5] Ágnes Timár-Balázsy, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann Series in Conservation and Museology (Oxford: Butterworth-Heinemann, 1998), 15–16, 23–25, 49–50.

Table 5-1 Monomer and chemical structure of cellulosic and proteinaceous fibres.[6,7,8]

	Cotton (cellulosic fibres)	Wool (proteinaceous fibres)
Monomer	Cellobiose, $C_{12}H_{20}O_{11}$, *(1-4)-β-D-glucopyranosyl-D-glucose*	Amino acid: Amine $-NH_2$ and Carboxylic acid $-COOH$
Crystallitniy (%)	65-80	25-30
Moisture regain (%) at 20 °C, 65 %RH	7-11	13.6-16.3
Water absorption (%)	8.5	15.0

(a)

(b)

Fig. 5-1 Chemical structure of cotton (a)[9] and wool (b)[10].

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[6] Boersma, *Unravelling Textiles*, 3.

[7] Naruse, *Basic Science of Clothing Material*, 22–25.

[8] Timár-Balázsy, *Chemical Principles of Textile Conservation*, 15–16, 23–25, 49–50.

[9] Kathryn L. Hatch, *Textile Science* (Minneapolis/Saint Paul, Minn: West Publishing Company, 1993), 166.

[10] Naruse, *Basic Science of Clothing Material*, 56.

5.3   Experimental

5.3.1   Materials

Plain-weave cotton fabric, 'cotton lawn' and plain-weave wool fabric 'wool delaine' were purchased from Whaleys (Bradford) Ltd. The thread counts of the cotton was 46 for warp $\times$ 60 for weft per 10 mm, and that of the wool was 26 for warp $\times$ 33 for weft per 10 mm, respectively. The fabrics selected in this research possess similar weights, thicknesses and thread counts with the pre-soiled fabrics used in Chapter 4.

Dehypon® LS45 was purchased from Conservation By Design Ltd. Dehypon® LS54 was supplied by BASF (Badische Anilin- und Soda-Fabrik) in Germany. The ramer® sponge (polyvinyl alcohol sponge) was purchased from Boots UK Ltd.

5.3.2   Sample preparation

To remove natural oils and/or substances added to ease the spinning or weaving processes, the wool delaine was scoured with 0.1% Dehypon® LS45 of detergent solution, the liquor to fabric ratio of 10:1, at 40 °C for 20 minutes, then rinsed in heated softened water lowering the temperature gradually to avoid causing felting. De-ionised water was used for the final rinse. The cotton lawn was scored at 90 °C for 133 minutes twice with Dehypon® LS45 in a washing machine, and ironed in order to remove dirt, oils and other water soluble impurities from manufacturing.

Each test fabric was cut to an 80 $\times$ 80 mm square, which allowed sufficient area needed for DRIFTs analysis.

For tensile testing, the test specimens were prepared following the British Standard Textiles- Tensile Properties of Fabrics (BS EN ISO 13934-1:1999).[11] The test specimens were cut to half the size of that outlined in the British Standard to give a dimension of 25 mm

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[11] *British Standard, Textiles - Tensile Properties of Fabrics, Part 1: Determination of Maximum Force and Elongation at Maximum Force Using the Strip Method BS EN ISO 13934-1:1999* (London: British Standard Institute, 1999).

width and a gauge length of 100 mm. An extra 25 mm was added to each end to allow enough fabric to be gripped in the jaws of the testing machine. A fringe of approximately 5 mm was also added to each side of the long edge (Fig. 5-2). In order to determine changes between detergents rather than assess the overall quality of the fabric, it was felt acceptable to use warp direction for this research. In accordance with the British Standard, the warps and wefts were sampled randomly, as shown in Fig. 5-2.
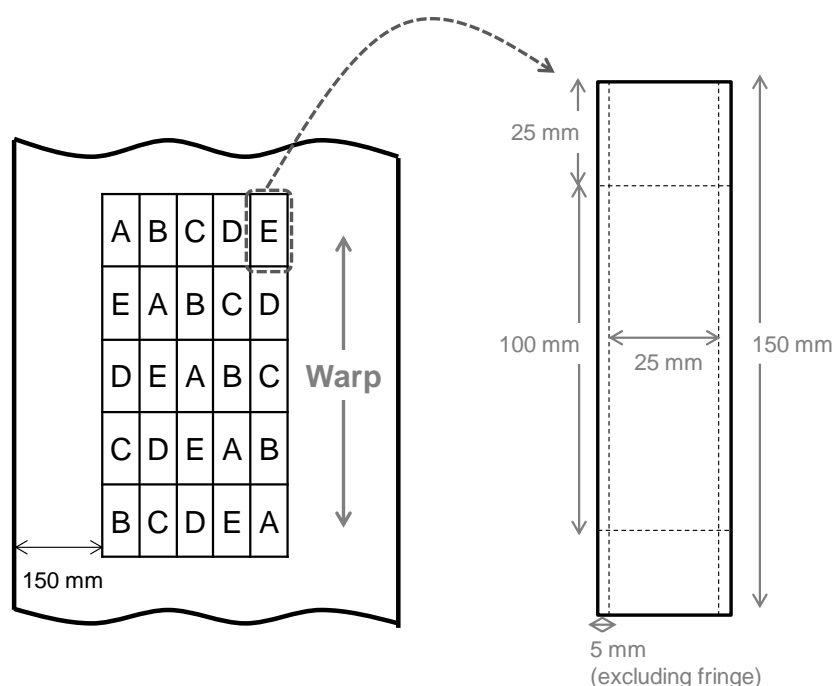
Fig. 5-2 Location of test specimens cut from fabric following British Standard.

5.3.3   Treatments

The wet-cleaning procedure used for this research is shown in Chapter 4, Table 4-3). Samples were pre-soaked in 250 ml of wash solution for two minutes and then washed by sponging twenty times for each sample every five minutes. This process was repeated twice before changing to a second fresh wash solution. Samples for unrinsed textile testing were then removed and dried on a Melinex® sheet without rinsing (Fig. 5-3). The remaining samples were then rinsed four times for five minutes with sponging each twenty times in softened water, and finally, were immersed in deionised water for two minutes. Both unrinsed and rinsed samples were placed on the Melinex® sheet to dry overnight before analysis. The

concentration of wash solution is shown in Table 5-2. The cmc value of LS45 was followed by Fields et al.[12] at 0.0598 %w/v. That of LS54 was calculated from the ratio of LS45 on the basis of the cmc values provided by BASF (see details in Chapter 2). For DRIFTs analysis and tensile test, ×5 cmc wash solution was used. As for preparation of experiment measuring thickness of fabrics, the concentration of wash solution ranged from ×5 CMC to ×20 CMC.
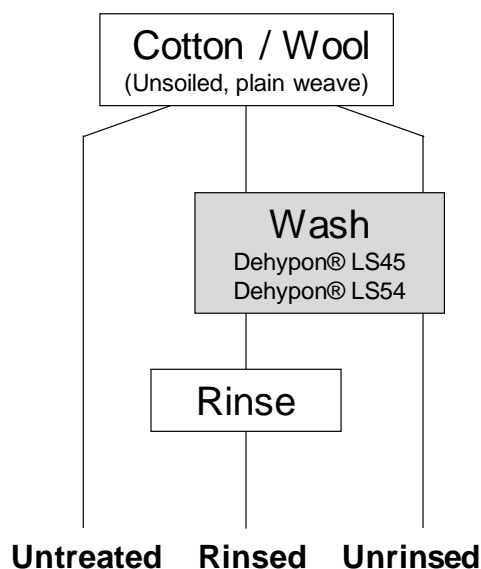
Fig. 5-3 A scheme of treatments process.

Table 5-2 Concentration of wash solution.

Dehypon®	Concentration (%w/v)			
	x5 cmc	x10 cmc	x15 cmc	x20 cmc
LS45	0.3	0.6	0.9	1.2
LS54	0.2	0.4	0.8	1

5.3.4   Measurements

5.3.4.1   DRIFTs

Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs) technique was undertaken with Dr. Leung Tang[13] at the University of Strathclyde, Department of Pure and

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[12] John A. Fields et al., "Finding Substitute Surfactants for Synperonic N," *Journal of the American Institute for Conservation* 43, no. 1 (2004): 55–73.

[13] Dr. Tang is application scientist (Mobile Measurement Chemical Analysis Group) at Agilent Technologies UK Limited in Edinburgh.

Applied Chemistry, using an Agilent 4100 ExoScan FTIR with the Diffuse Reflectance equipped with Temperature controlled DTGS (deu-terated triglycine sulfate) detector. Spectra within the range of 4500 to 650 cm^{-1} were collected at a resolution of 8 cm^{-1} and 128 scans. The DRIFTs data were processed using Panorama (LabCognition Inc., Germany) software. Using the standard method for analysing liquids by infra-red spectroscopy, a thin layer of neat solution of Dehypon® LS45 and Dehypon® LS54 was applied to an aluminium plate, and after drying, the analysis was undertaken for five times. The aluminium plate was cleaned by acetone before each experiment. In terms of analysis of fabric, the flat surface of the fabric was maintained with an aluminium substrate (Fig. 5-4) and five points of each fabric in front and back was analysed.

Fig. 5-4 DRIFTs analysis of a fabric.

5.3.4.2 Thickness

Measurement of thickness of the fabrics is one of the simplest ways to ascertain how the fibres are swelling or shrinking by the washing process as well as remaining residues. The thickness of fabric was measured using a Digital External Micrometer 0-25 mm with accuracy of 0.001 mm (SEALEY, Model No. AK9635D) (Fig. 5-5). The measurements were conducted for ten points of each fabric. The statistical significance of the differences between wet cleaning treatments (rinsed and unrinsed) and thickness of fabrics was investigated by Student's t-test. In all evaluations, a significant difference was accepted at a value of $P < 0.05$

(see detail in Appendix 4).

Fig. 5-5 Measuring the thickness of fabric.

5.3.4.3   Tensile Test

In order to detect whether the residues of LS45 and LS54 affected the fibres tensile properties, a tensile test was carried out at the CTCTAH using an Instron[®] 5544 Tensile Tester and Instron Bluehill software version 1.4 (Instron Corp. Canton, MA) with a 1 kN load cell at an extension rate of 100 mm/min (Fig. 5-6). In each measurement, five specimens were used for breaking extension (the distortion until specimen is broken (mm)) and load at break (tensile force required to break the specimen (N)). The environment throughout the testing ranged from 23-24 °C and 37-38% RH. The statistical significance of the differences between wet cleaning treatments (rinsed and unrinsed) and tensile strengths and strains was investigated by Student's *t*-test as described above (Thickness).

Treatment caused no macroscopically visible change to the samples. It was necessary to examine them at high magnification to determine whether any microscopic differences could be detected between treated samples and untreated controls. This would help determine if any residues had deposited or if fibres appeared dessicated after treatment.
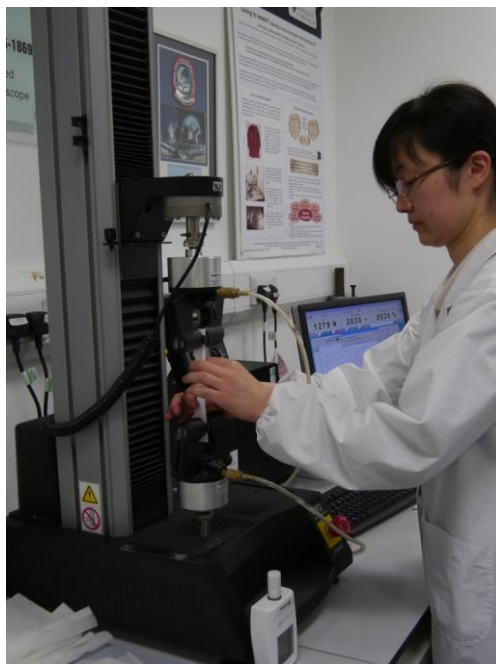
Fig. 5-6 Setting a specimen for tensile test.

5.3.4.4　SEM observation

SEM observation can help determine whether any residues had deposited or if fibres were caused damage such as abrasion after wet cleaning. Observation of the fabric and fibre surface before and after wet cleaning was undertaken using a Hitachi S-4200 Field Emission Scanning Electron Microscope (FE-SEM) with a range from at the Kyoto Institute of Technology in Japan.[14] The magnifications were ×100, ×300 and ×5000 and acceleration voltage was at 8.0 kV.　All the fibres were gold coated using ion sputtering equipment (JEOL Ltd., JFC-1100E) at 6 mA for four minutes prior to the FE-SEM measurement.

5.4　Results and discussion

5.4.1　DRIFTs

5.4.1.1　Fabrics

Repeatability of the measurements was ensured by analysing cotton reference fabric at a point for nine times. Fig. 5-7 shows nine scans of DRIFT spectra of cotton, within the region

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[14] The SEM observation was supported by Ph.D Candidate Mr. Keisuke Maeda at the Kyoto Institute of Technology, Japan.

5000 cm^{-1} to 950 cm^{-1}. As shown in the detail spectra of Fig. 5-8, the absorption of -OH free stretching at 3458 cm^{-1} and –OH bending at 1634 cm^{-1} was decreased over time and this was because of moisture absorption and desorption of fibres. On the other hand, other characteristic bands of cotton were stable. It was therefore considered that the DRIFT analysis of the fabric was acceptably reproducible.

Untreated cotton and wool fabrics were firstly analysed. Characteristic spectral bands assigned are presented in Fig. 5-9 and Table 5-3 for cotton, and Fig. 5-11 and Table 5-4 for wool.
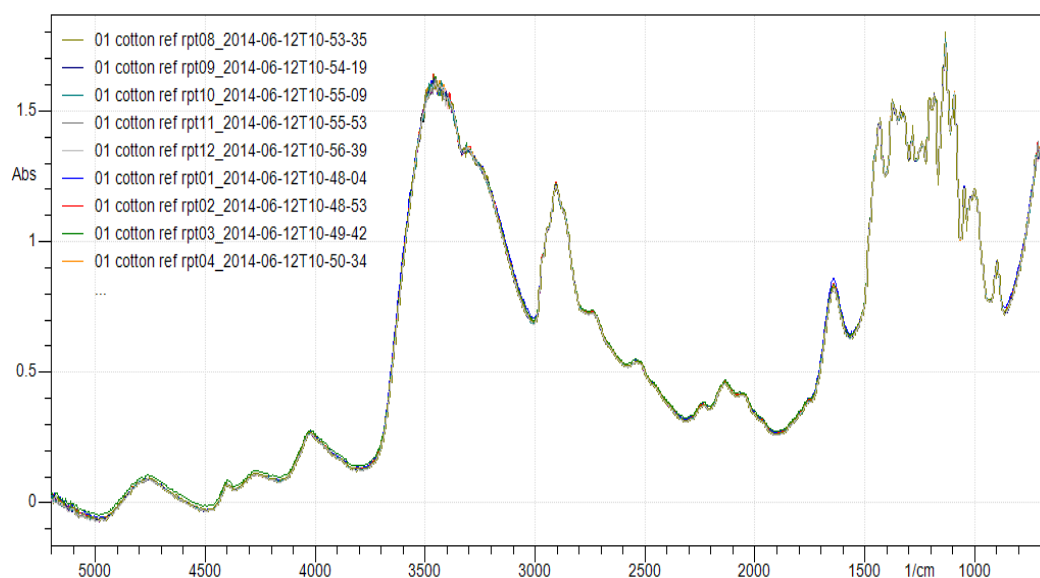
Fig. 5-7 DRIFT spectra of repeatability test for untreated cotton in the region 5200-650 cm^{-1}.
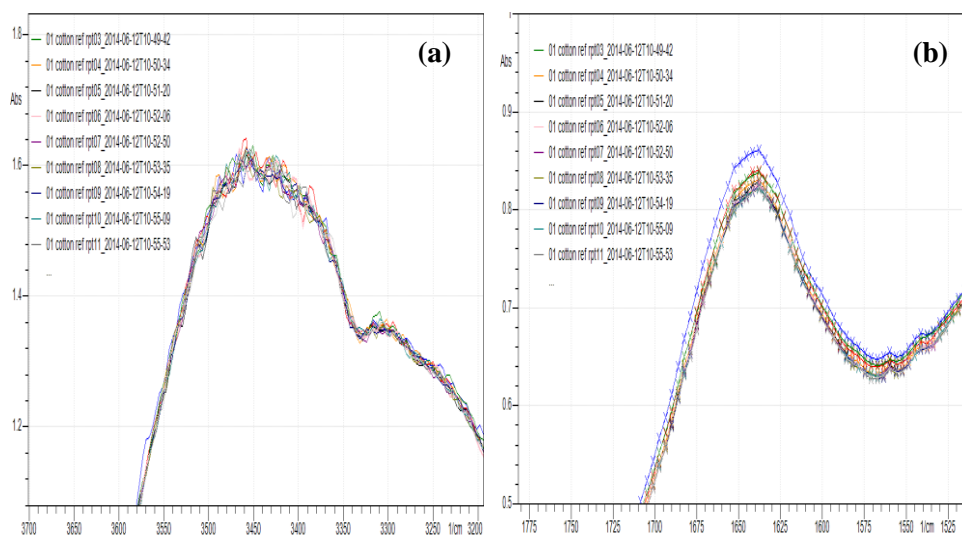
Fig. 5-8 Repeatability test of cotton in the region 3700-3200 cm^{-1} (a) and 1775-1510 cm^{-1} (b).
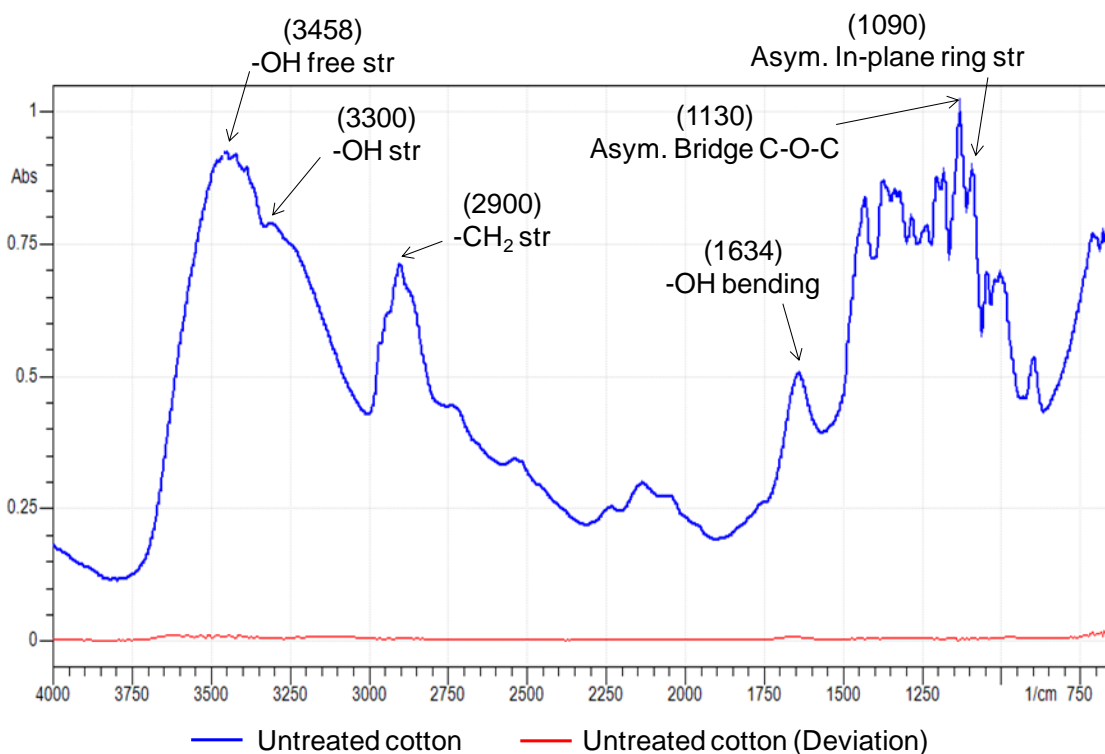
Fig. 5-9 Average DRIFT spectra of untreated cotton in the region 4000-650 cm^{-1}.

Table 5-3 Infrared absorption frequencies of cotton reference fabric.[15]

Weavemark (cm^{-1})	Assignment	Comment
3458	-OH free str	Intra-molecular -OH
3300	-OH str	Intermolecular -OH
2900	-CH$_2$ str	Asym. CH$_2$ stretch: long alkyl chain
1634	-OH bending	Adsorbed H$_2$O
1130	C-O-C	Asym. Bridge C-O-C
1090		Asym. In-plane ring str.
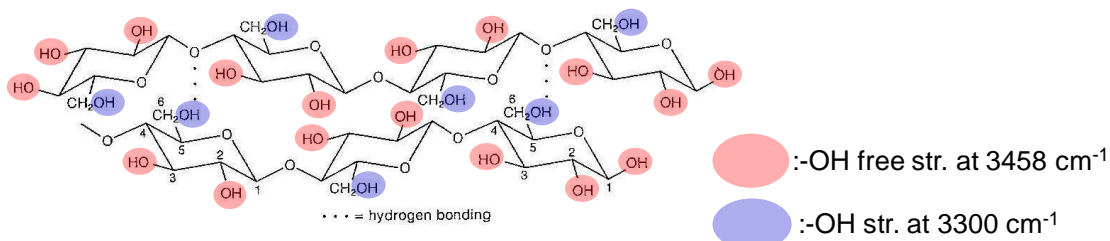
Fig. 5-10 Intra-molecular hydrogen bonds intermolecular hydrogen bounds presenting in the polymer of cotton. (Image taken and modified from Hatch[16])

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[15] Chinkap Chung, Myunghee Lee, and Eun Kyung Choe, "Characterization of Cotton Fabric Scouring by FT-IR ATR Spectroscopy," *Carbohydrate Polymers* 58, no. 4 (7 2004): 417–20, doi:10.1016/j.carbpol.2004.08.005.

[16] Hatch, *Textile Science*, 166.
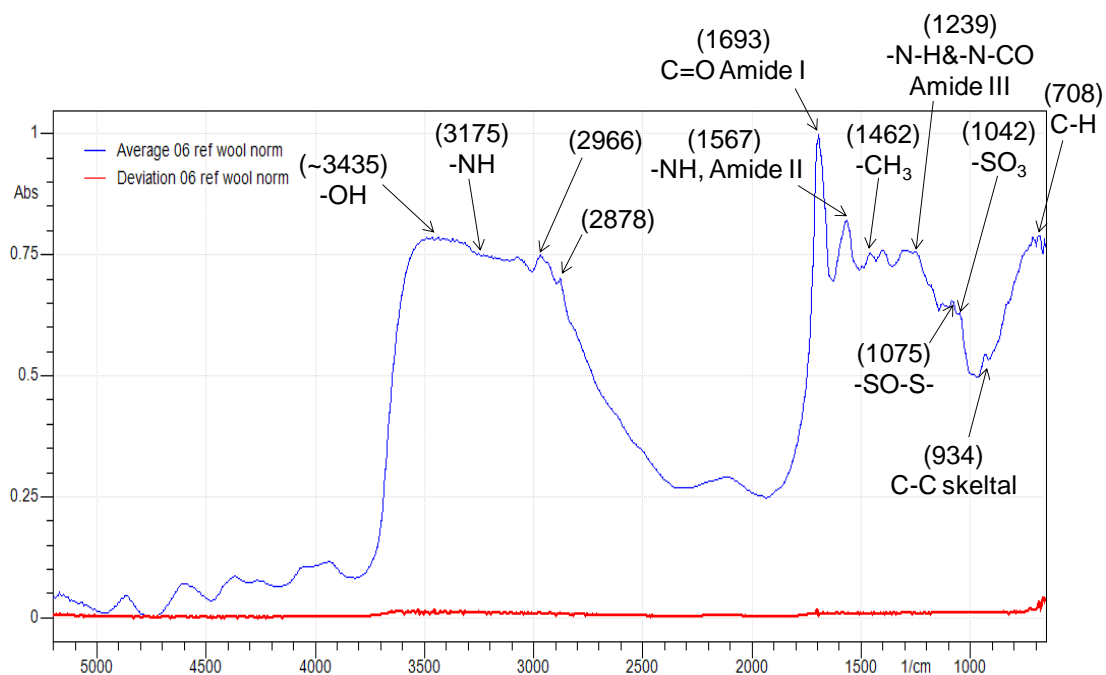
Fig. 5-11 DRIFT spectra of untreated wool.

Table 5-4 Infrared absorption frequencies of wool reference fabric.[17]

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[17] Marianne Odlyha, Charis Theodorakopoulos, and Roberto Campana, "Studies on Woolen Threads from Historical Tapestries," *AUTEX Research Journal* 7, no. 1 (March 2007): 9–18.

For cotton fabric, the -OH free stretching at 3458 cm^{-1} is attributed to intra-molecular hydrogen bonds, whereas -OH free stretching at 3300 cm^{-1} is attributed to intermolecular hydrogen bonds from water (Fig. 5-10).[18] They account for the main hydrogen bonding present in the polymer of cotton. A peak at 2900 cm^{-1} corresponds to the asymmetric –CH$_2$ stretching in long alkyl chain. A peak at 1634 cm^{-1} would be due to the adsorbed water molecules.[19] A peak at 1130 cm^{-1} is an asymmetric bridge C-O-C of cellulose chain. A peak at 1090 cm^{-1} is due to the C–O stretch of cellulose chain and asymmetric in-plane ring stretch.[20]

In untreated wool, characteristic bands of proteins appear (Fig. 5-11): Amide I at 1693 cm^{-1}, indicating alpha-helical structures, is mainly associated with the C=O stretching vibration and is directly related to the backbone conformation; Amide II at 1567 cm^{-1} corresponds to N-H bending and C-N stretching vibrations; and Amide III at 1239 cm^{-1} corresponds to the in-phase combination of C-N stretching and N-H bending, with some contribution from C-C stretching and C=O bending vibrations. The latter is a complex band, and depends on the nature of side chains and hydrogen bonding, which is in the nature of wool.[21]

5.4.1.2 Dehypon® LS45 and LS54

Fig. 5-12 shows DRIFT spectra of neat solution of Dehypon® LS45 (LS45) and Dehypon® LS54 (LS54), within the region 5000 cm^{-1} to 650 cm^{-1}, after baseline correction and normalization using the spectroscopy software. Characteristic bands of both detergents were analysed and listed in Table 5-5. In the both LS45 and LS54, characteristic bands of

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[18] Jamaliah Md Jahim Ario Betha Juanssil Fero, "Application of the Aqueous Two-Phase Thermoseparating Systems of Dehypon® LS 54-the Waxy Maize Starch for Protein Extraction," *Journal of Applied Sciences*, 2010, 95, doi:10.3923/jas.2010.2596.2601.

[19] Chung, Lee, and Choe, "Characterization of Cotton Fabric Scouring by FT-IR ATR Spectroscopy."

[20] Chung, Lee, and Choe.

[21] Odlyha, Theodorakopoulos, and Campana, "Studies on Woolen Threads from Historical Tapestries."

hydrophobic and hydrophilic appear: peaks at 3591 cm^{-1} and 3482 cm^{-1} are attributed to the -OH free stretching and -OH stretching, respectively. These peaks would be related to the end of the hydroxyl group in the hydrophilic part (see Chapter 2, Fig. 2-2); Asymmetric -CH$_2$ stretching at 2926 cm^{-1} and symmetric -CH$_2$ stretching at 2858 cm^{-1} correspond to fatty alcohol, ethylene oxide (EO) and propylene oxide (PO), whereas –CH$_3$ stretching at 2967 cm^{-1} and -CH$_3$ deformation vibration at 1459 cm^{-1} and 1372 cm^{-1} are associated with PO; C-O-C stretching vibration at 1115 cm^{-1} corresponds to aliphatic ethers in EO and PO; (CH$_2$)$_n$, n$\geq$4 at 722 cm^{-1} is uniquely associated with fatty alcohol.
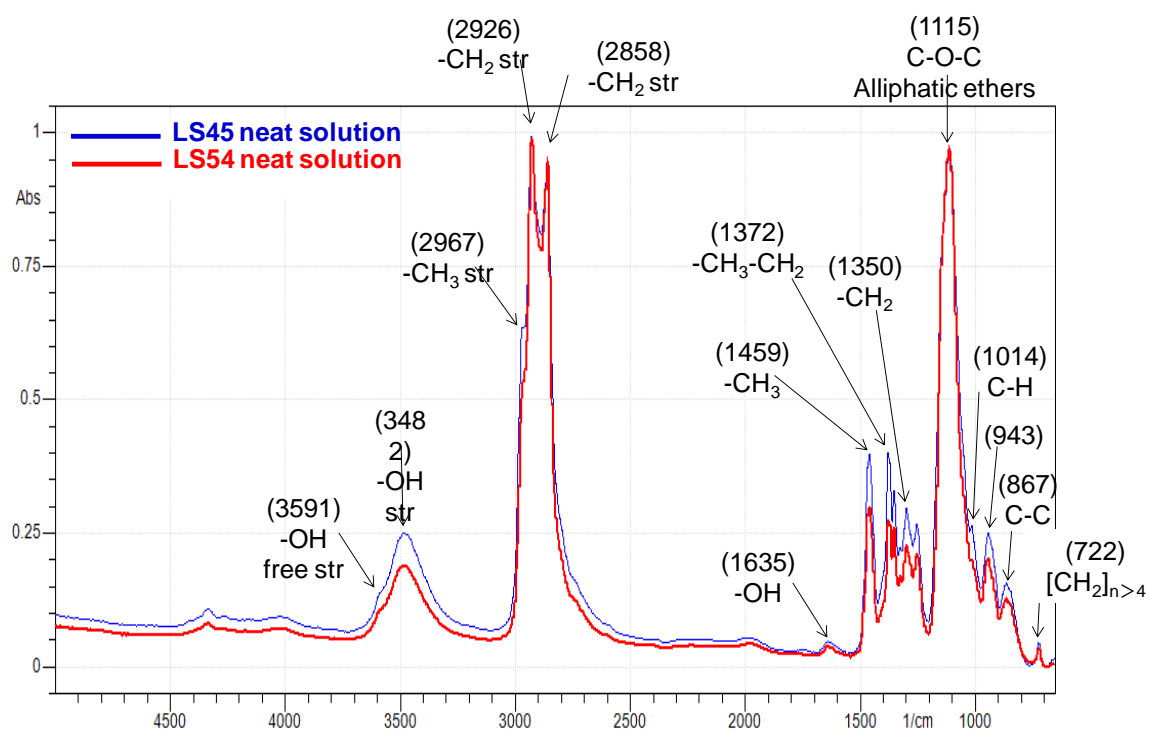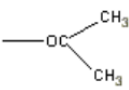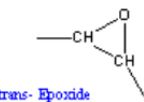
Fig. 5-12 DRIFT spectra of neat solution of Dehypon® LS45 and Dehypon® LS54 in the region 5000 cm^{-1} to 650 cm^{-1},.

Table 5-5 Characteristic IR frequencies of Dehypon® LS45 and Dehypon® LS54.

Weavemark (cm^{-1})	Assignment	Comment
3591	-OH free str	
3482	Associated -OH str	
2967	$-CH_3$ str	
2926	$-CH_2$ str	Asymetric $-CH_2$
2907	-CH	
2900	-CH	
2870	$-CH_3$	
2858	$-CH_2$ str	Symetric $-CH_2$
1635	-OH bending	
1459	$-CH_3$	
1372	$-CH_3$	
1372	$-CH_2$	
1350	$-CH_2$ -OH	Secondary alcohol
1298	CH_4-OH	
1160	$CH_2-\overset{\overset{CH_3}{\mid}}{CH}$	
1147	C-O-C	Alliphatic ethers EO based
1115	C-O-C	Alliphatic ethers PO based
1014	—OC(CH_3)(CH_3)	Side reaction (?) C-H deformation vibration
943	trans- Epoxide	Unreacted Epoxide ring vibration
867	▷	C-C skeleton vibration
838	C(CH_3)(CH_3)	C-C skeletal vibration
722	$(CH_2)_n$	$n \geqq 4$

In order to clarify the spectral differences between LS45 and LS54, the averaged spectra of LS54 was subtracted from that of LS45 (Figs. 5-13 and 5-14). From the subtracted spectra, it is considered that LS45 has more –OH, -CH$_3$ and (CH$_2$)$_n$, n≥4 than LS54 (Fig. 5-15 and Table 5-6). The reason for a more –OH group in LS45 might be Dehypon$^®$. LS54 is made as a more condensed surfactant than LS45 during the manufacturing process. Having more –CH$_3$ in LS45 is in agreement with an already-known value for PO, which is 5 moles for LS45 and 4 moles for LS54 (see Chapter 2, Table 2-2). In addition, it is considered that LS45 would have a longer fatty alcohol chain segment than LS54, as it has a higher absorbance at 722 cm^{-1} associated with (CH$_2$)$_n$, n≥4.
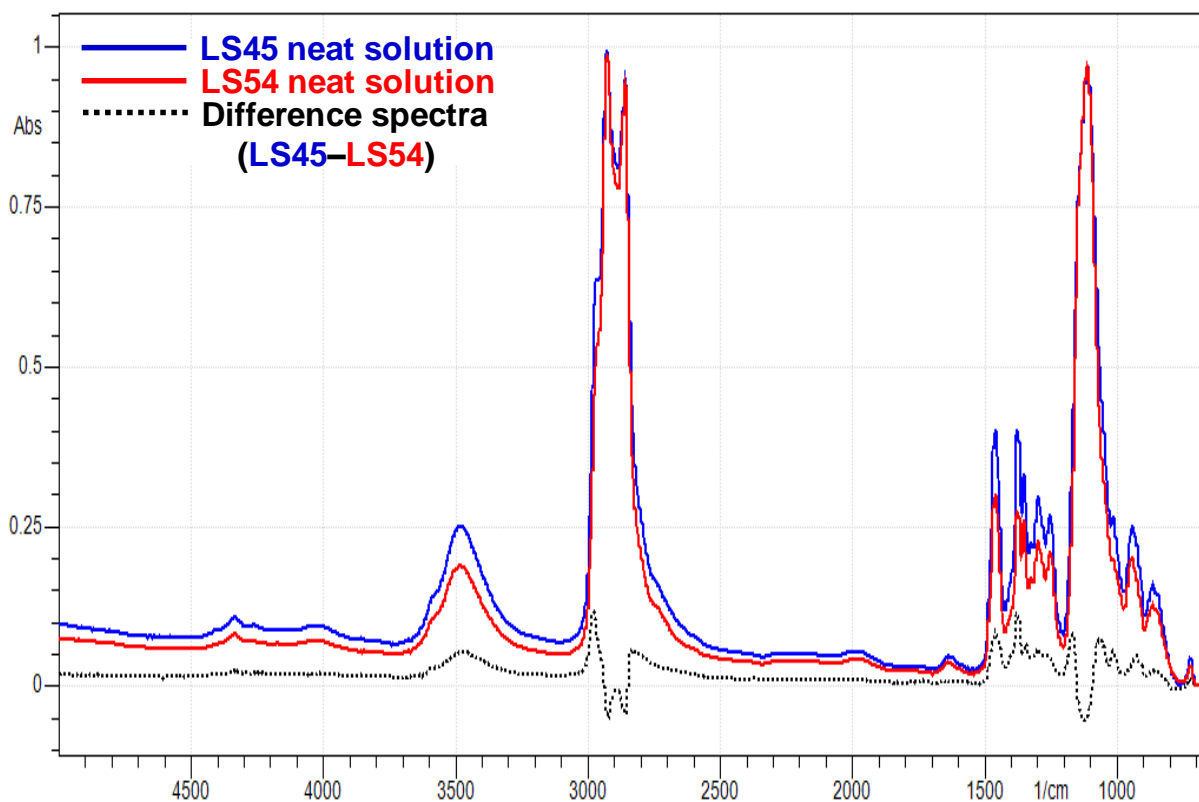
Fig. 5-13 DRIFT spectra and Difference spectra of neat solution of Dehypon$^®$ LS45 and Dehypon$^®$ LS54. In Difference spectra, the spectra of LS54 were subtracted from that of LS45.
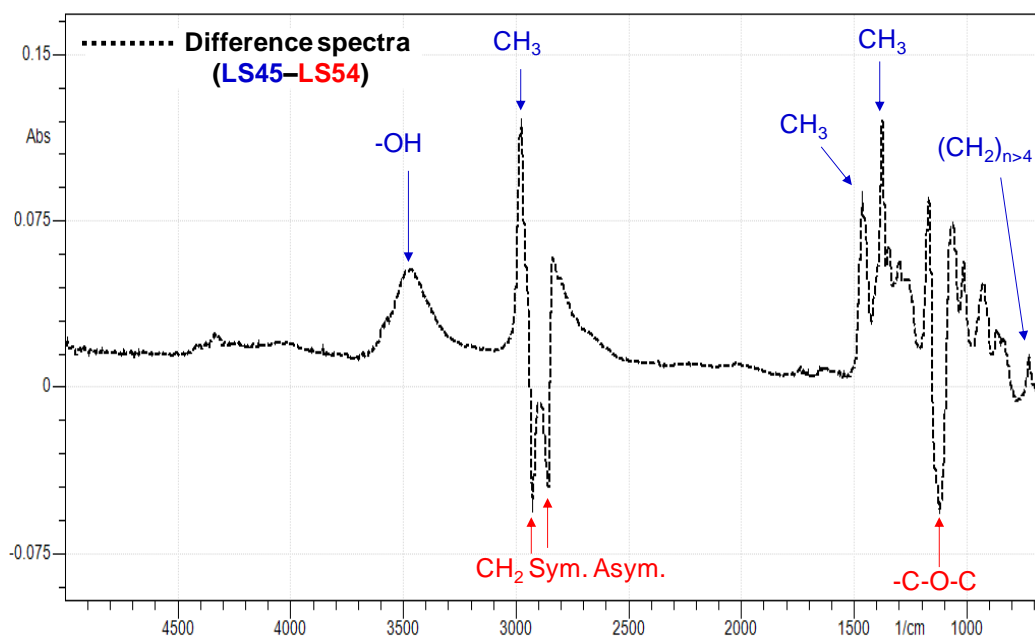
Fig. 5-14 Difference spectra of neat solution of Dehypon® LS45 and Dehypon® LS54. In Difference spectra, the spectra of LS54 were subtracted from that of LS45.
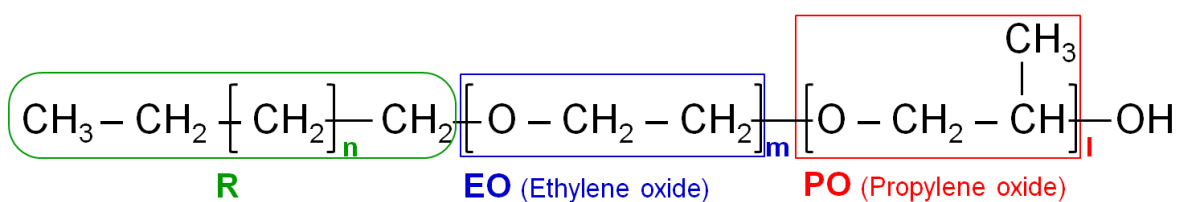
Fig. 5-15 The chemical structure of alcohol EO/PO adducts.

Table 5-6 Summary of Difference spectra of neat solution of Dehypon® LS45 and LS54 by DRIFTs analysis.

	Dehypon® LS45 R—EO$_4$—PO$_5$—OH	Dehypon® LS54 R—EO$_5$—PO$_4$—OH
-OH	More	Less
-CH$_3$	More	Less
(CH$_2$)$_{n>4}$	More	Less
-CH$_2$	Less	More
C-O-C	Less	More

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It is considered that the higher the number of EO, the greater the cloud point of the detergent and also the greater its hydrophilic character. This is because the hydrophilic properties of non-ionic surfactant are conferred by the presence of oxygen atoms which are capable of forming hydrogen bonds with molecules of water.[22] As the temperature of the surfactant solution is increased the hydrogen bonds gradually break causing the surfactant to emerge from the solution at the cloud point (Fig. 5-16).[23,24] Since LS54 has more C-O-C than LS45, LS54 would be more hydrophilic and hence retain more water, releasing it at a higher cloud point than LS45.
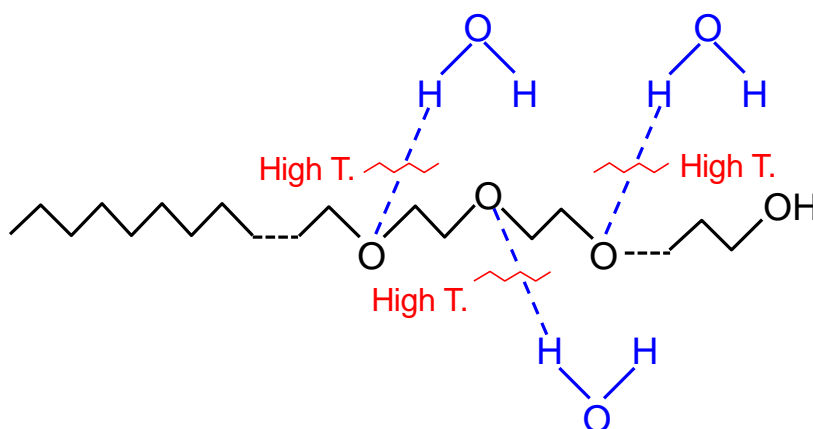
Fig. 5-16 Representation of hydrogen bonds between ether group in Dehypon® LS45 and LS54 and molecules of water, which are broken above the cloud point.

Furthermore, as pointed out in Chapter 3, although LS54 has higher cloud point and is more hydrophilic due to lower number of PO (propylene oxide), cmc of LS54 is lower than LS45. In general, a surfactant that has higher cmc tends to have a higher cloud point, more hydrophilic character and longer alkyl chain than a surfactant having a lower cmc.[25,26] The

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[22] Hans Schott, "Hydrophile-Lipophile Balance and Cloud Points of Nonionic Surfactants," *Journal of Pharmaceutical Sciences* 58, no. 12 (Spring 1969): 1443–49, doi:10.1002/jps.2600581203.
[23] Ágnes Tímár Balázsy, "Wet Cleaning of Historical Textiles: Surfactants and Other Wash Bath Additives," *Reviews in Conservation* 1 (2000): 52.
[24] "Surfactants," accessed July 5, 2014, http://www.essentialchemicalindustry.org/materials-and-applications/surfactants.html.
[25] Matthew A. Cowell et al., "Partitioning of Ethoxylated Nonionic Surfactants in Water/NAPL Systems: Effects of Surfactant and NAPL Properties," *Environmental Science & Technology* 34, no. 8 (Spring 2000): 1587, doi:10.1021/es9908826.
[26] Tianhong Zhang and Roger E. Marchant, "Novel Polysaccharide Surfactants: The Effect of Hydrophobic and Hydrophilic Chain Length on Surface Active Properties," *Journal of Colloid and*

higher cmc value of LS45 can be proved that LS45 would have a longer fatty alcohol chain due to the higher the number of $(CH_2)_n$, $n \geq 4$.

5.4.1.3 Treated fabrics

During the wet cleaning process, sponging treatment was carried out just for the front of the fabrics. In order to clarify the spectra difference between front and back, both sides of the fabrics were analysed. As shown in the spectra of the front and back of both cotton and wool, which were washed with LS45 and then rinsed with soften water (Figs. 5-17 and 5-18), there are no detectable significant differences. This was a useful result as it is considered that the same washing effect may be received at the level of spectroscopic analysis. Therefore for further testing it was decided to use the spectra obtained from the front of fabrics.

Fig. 5-19 gives DRIFT spectra of: (a) untreated cotton, (b) washed and rinsed cotton and (c) washed but unrinsed cotton, within the region 4000 cm^{-1} to 650 cm^{-1}. In this example the baseline needed to be corrected by the software in order to account for diffusion differences. Fig. 5-20 shows the spectrum of them in the region 750-650 cm^{-1}.

Fig. 5-21 gives DRIFT spectra of untreated wool, washed and rinsed wool and washed but unrinsed wool, within the region 3700 cm^{-1} to 650 cm^{-1}. The baseline was corrected because of diffusivity differences. From Fig. 5-22, they show the spectrum of them in the region 780-670 cm^{-1}. As explained above in the results of LS45 and LS54 neat solution, $(CH_2)_n$, $n \geq 4$ at 722 cm^{-1} is uniquely associated with fatty alcohol of these surfactants. At 710 cm^{-1} for cotton and 707 cm^{-1} for wool, it is considered that these peaks are associated with fatty alcohol of LS45 and LS54. As shown in Fig. 5-20 and 5-22, except cotton washed by LS54, the peak of unrinsed fabric was noticeably detected at 710 cm^{-1} and 707 cm^{-1} , respectively. Therefore, it is considered that DRIFTs technique has a possibility of detecting surfactant residue on cotton and wool when they were not rinsed.
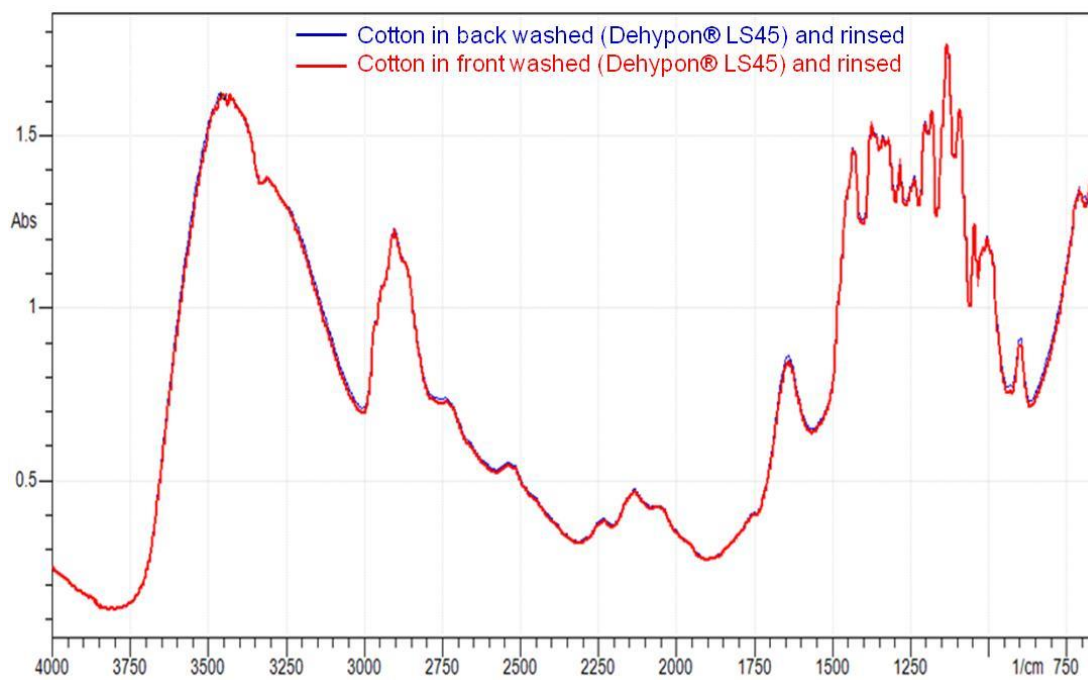
Fig. 5-17 DRIFT spectra of cotton in back and front washed (Dehypon® LS45) and rinsed.
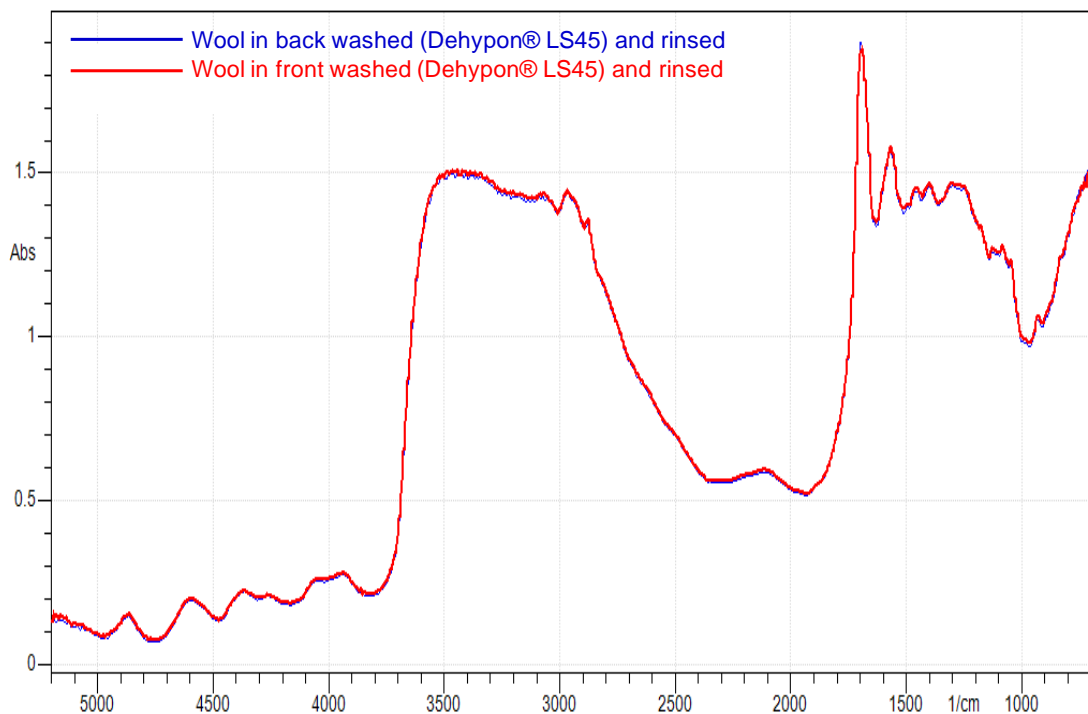
Fig. 5-18 DRIFT spectra of wool in back and front washed (Dehypon® LS45) and rinsed.
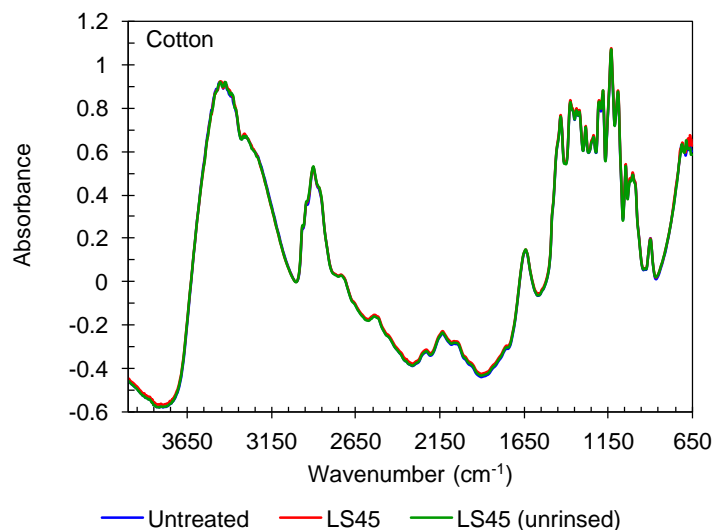
Fig. 5-19 DRIFT spectra of cotton washed (Dehypon® LS45) and rinsed or unrinsed in the region 4000-650 cm⁻¹.
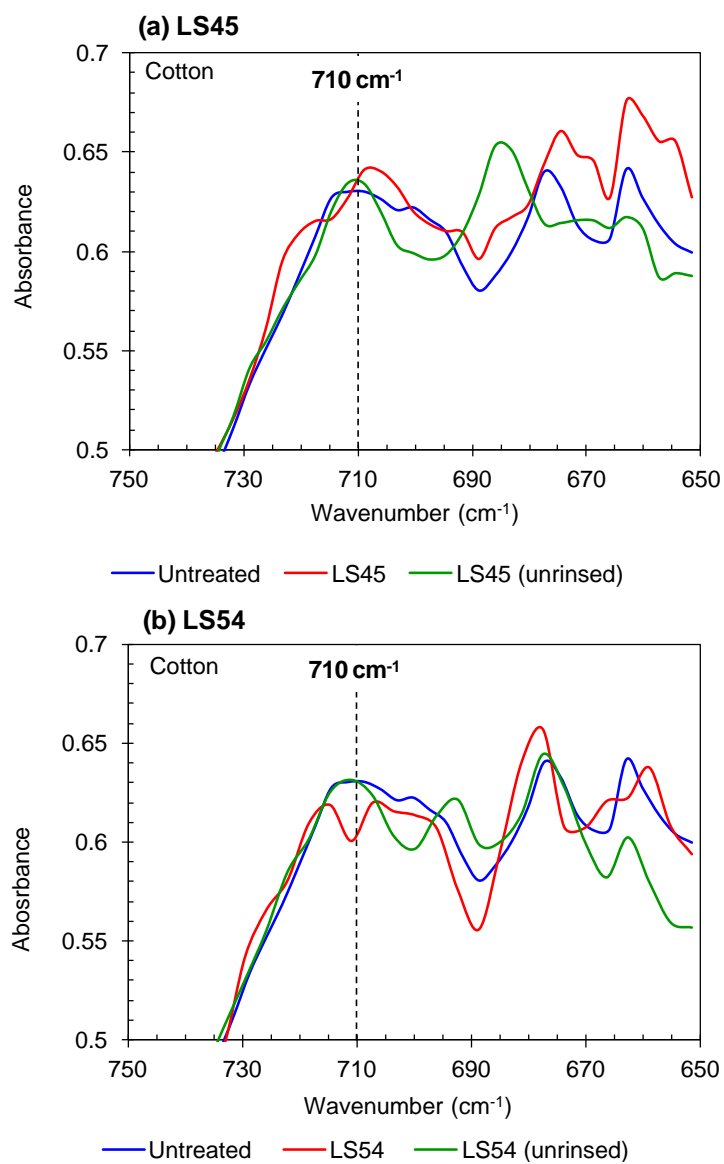
Fig. 5-20 DRIFT spectra of cotton washed by Dehypon® LS45 (a) and LS54 (b), and rinsed or unrinsed in the region 750-650 cm⁻¹.
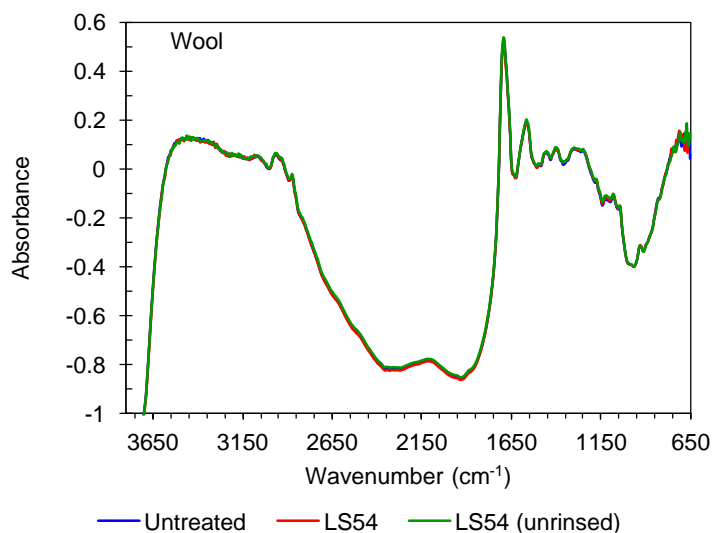
Fig. 5-21 DRIFT spectra of wool washed by Dehypon® LS45, and rinsed or unrinsed in the region 3700-650 cm^{-1}.
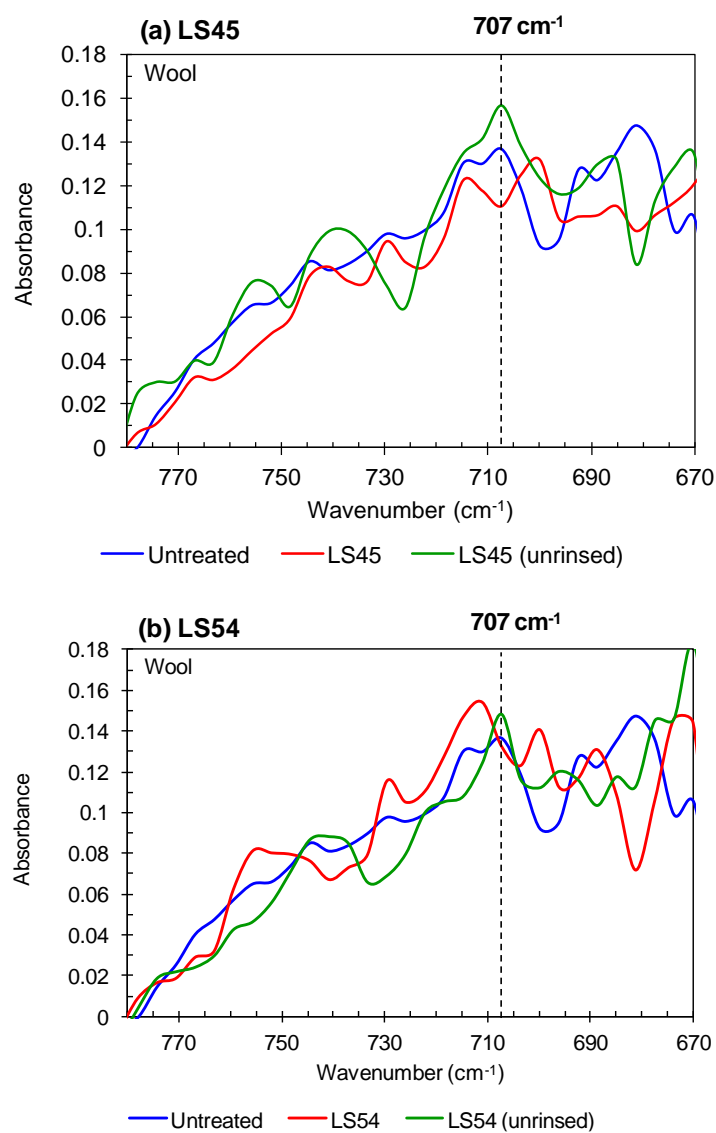
Fig. 5-22 DRIFT spectra of wool washed by Dehypon® LS45 (a) and LS54 (b), and rinsed or unrinsed in the region 780-670 cm^{-1}.

5.4.2 Thickness

A measurement of fabric thickness was carried out to physically determine the swelling of fabric after wet cleaning treatment with, and without, rinsing. Fig. 5-23 give the thickness of cotton and wool after washing with LS45 and LS54. There was no change between untreated samples and one washed through the concentrations between 0.3% and 12%.
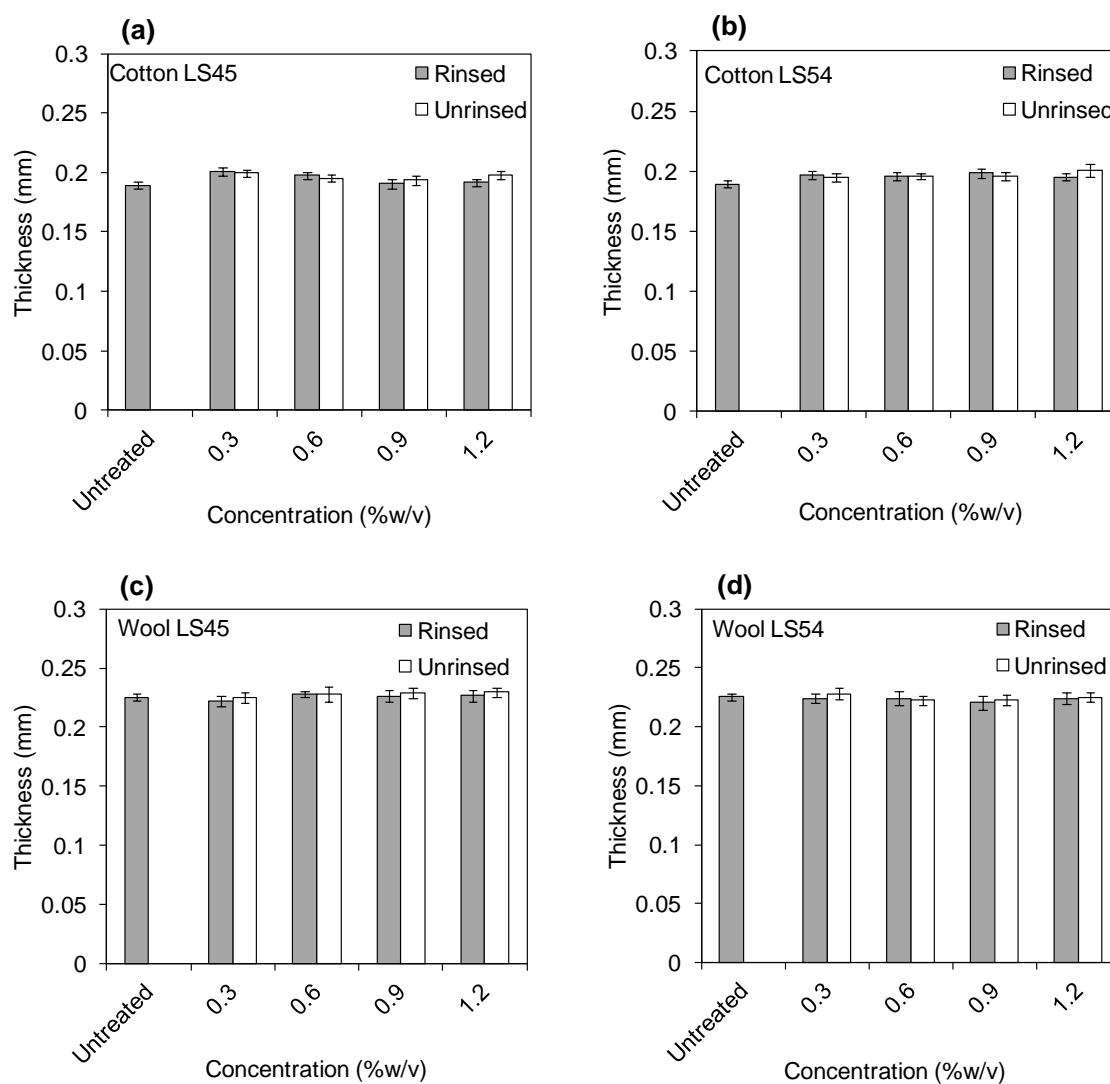
Fig. 5-23 Thickness of cotton (a) (b) and wool (c) (d) before and after wet cleaning by Dehypon®
LS45 and LS54 with or without rinsing.

5.4.3 Tensile Test

Figs. 5-24 and 5-25 show typical load-extension curves for the cotton and wool after the wet cleaning treatment with LS45 and LS54. The load at break and breaking extension results were plotted against each treatment in Fig. 5-26. The cotton and wool after all treatments showed similar mechanical strength with untreated samples, while the breaking extension of wool after treatments was slightly greater than that of untreated wool.

In order to compare the differences between cotton and wool in rinsed and unrinsed experiments and untreated samples, the changing rate of load at break and breaking extension after each treatment was calculated by the following equation (1), and the results are shown in Fig. 5-27. This calculation can enable comparison between the tensile property among different fabrics and surfactants.

$$\text{Changing Rate (\%)} = \frac{\text{Bt (Lt)} - B_0 \text{ (L}_0\text{)}}{B_0 \text{ (L}_0\text{)}} \times 100 \qquad (1)$$

Bt = Breaking Extension of the treated sample, Lt = Load at Break of the treated sample
B_0 = Breaking Extension of the untreated sample, L_0 = Load at Break of the untreated sample

As for cotton, both load at break and breaking extension on all treated samples was not changed and was maintained at 0%. This result shows that wet cleaning with LS45 and LS54 and their residues did not significantly affect the mechanical property of cotton fibre as tested by this method. In terms of wool, although the changing rate of load at break was not changed from untreated samples through the all treatments, the breaking extension was considered to be influenced by all treatments. The breaking extension of wool washed only by water increased by 20% and that of wool washed with LS45 and LS54 and rinsed showed a similar increased amount at 20%. On the contrary, unrinsed wool washed by LS45 and LS54 increased by approximately 50% on their breaking extension. These results suggest that residues of LS45 and LS54 may change the mechanical properties of wool, so it is concluded that the rinsing process is vital for wet cleaning of wool. Additional testing is recommended

to understand physical properties between surfactants and fibres.
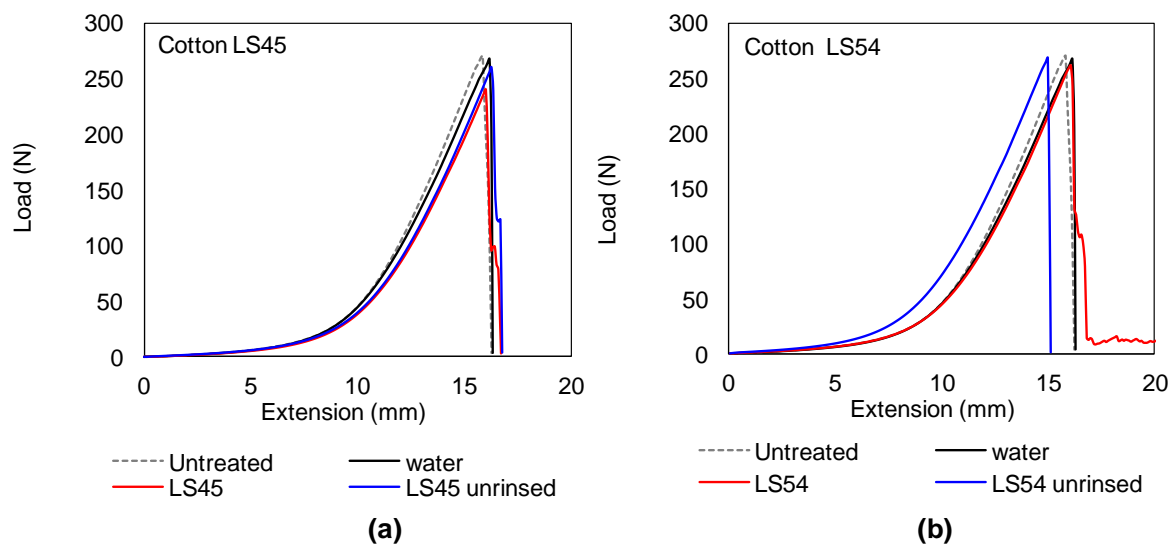
Fig. 5-24 Load-extension curves of the cotton after the wet cleaning treatment with LS45 (a) and LS54 (b).
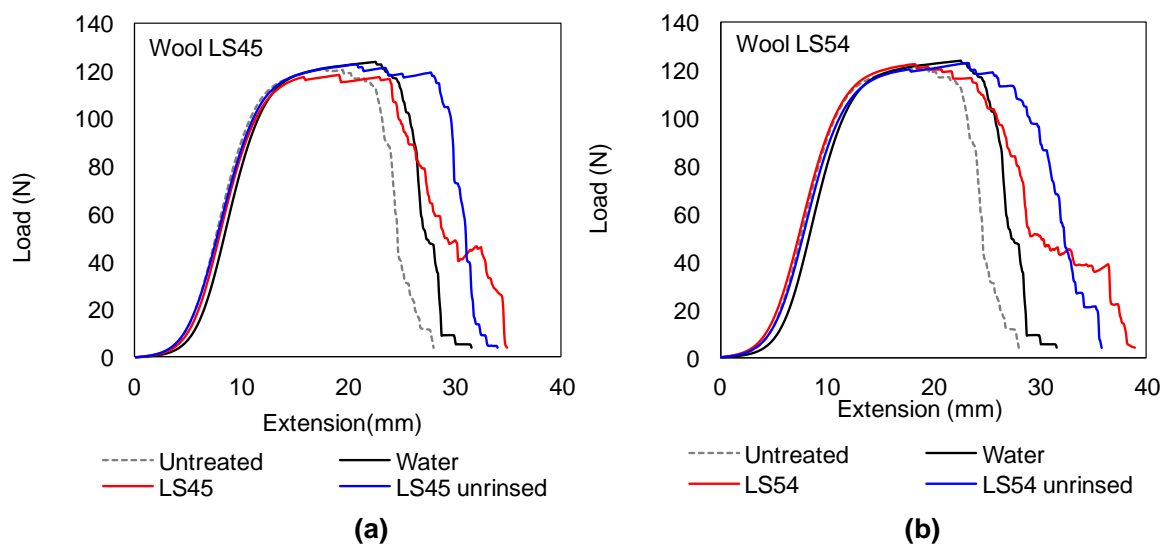
Fig. 5-25 Load-extension curves of the wool after the wet cleaning treatment with LS45 (a) and LS54 (b).
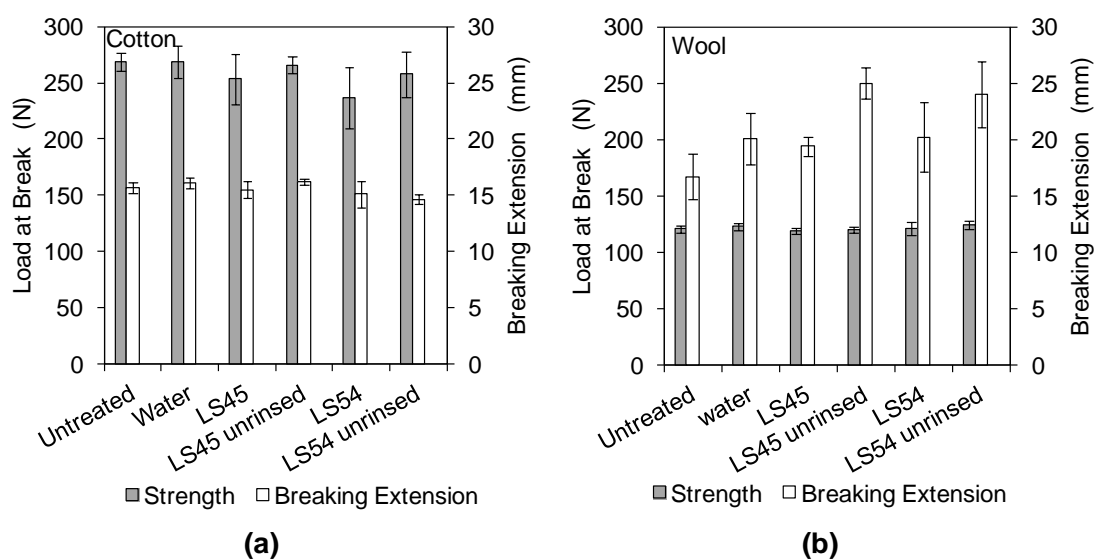
Fig. 5-26 Treatment-dependence of load at break and breaking extension for cotton (a) and wool (b).
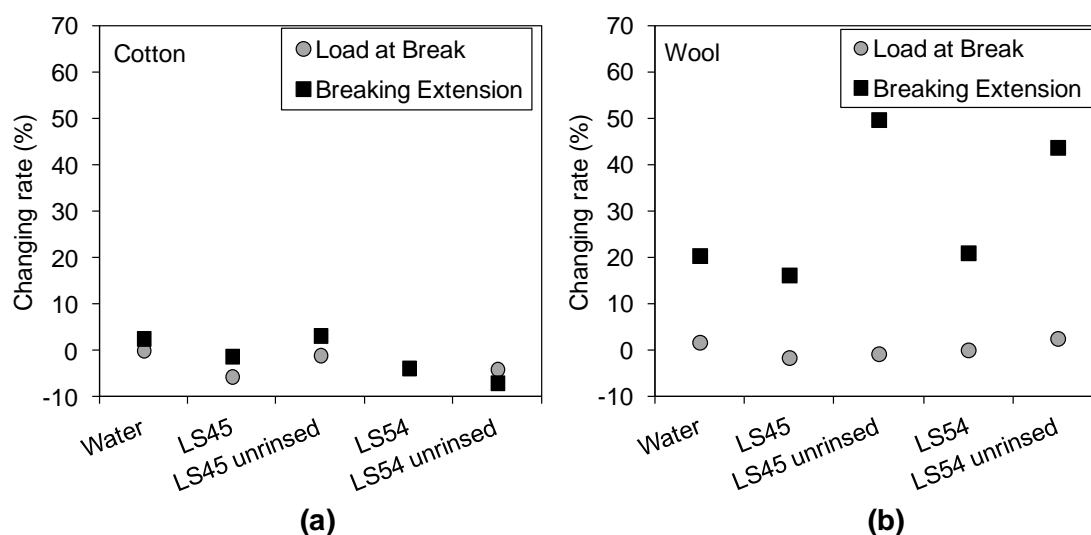
Fig. 5-27 Changing rate of load at break and breaking extension for cotton (a) and wool (b).

5.4.4 SEM Observation

A SEM was used to observe the change in the fibre surface morphology after wet cleaning at the microscopic level. Figs 5-28 and 5-29 show SEM micrographs of the surface morphology of the cotton and wool washed by LS54 with and without rinsing. Compared to the untreated cotton (Fig. 5-28 (a)), the washed cotton samples (Figs 5-28 (b) and (c) at 300× magnification) show abrasions on their surface of fibre. This might be caused by hand

sponging during wet cleaning. Furthermore, the washed cotton samples appeared to have residues on their fibre surface (Figs. 5-28 (b) and (c) at 5000× magnification). As for the SEM micrographs of surface morphology of the wool (Figs. 5-29 (b) and (c)), the scale became slightly smoother than the untreated wool. It was also considered that the mechanical agitation by hand sponging may cause damages on the surface of the wool. There was no apparent difference in the surface morphology of the untreated wool and washed and then rinsed wool, while a small amount of residue can be seen on the surface of unrinsed wool.
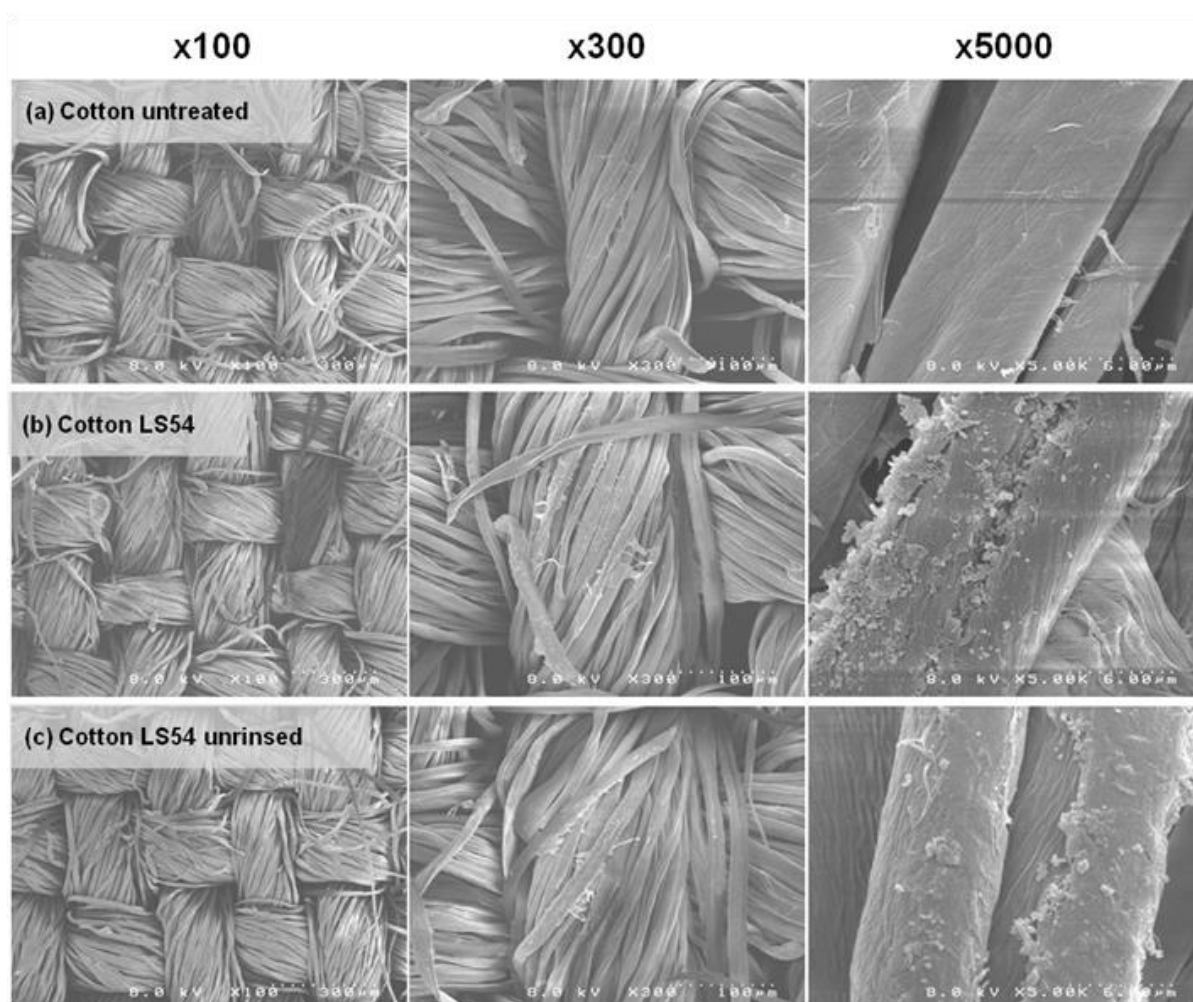
Fig. 5-28 SEM micrographs of cotton surface before (a) and after washed by LS54 with (b) and without rinsing (c). The magnifications were ×100, ×500 and ×5000 (left to right).
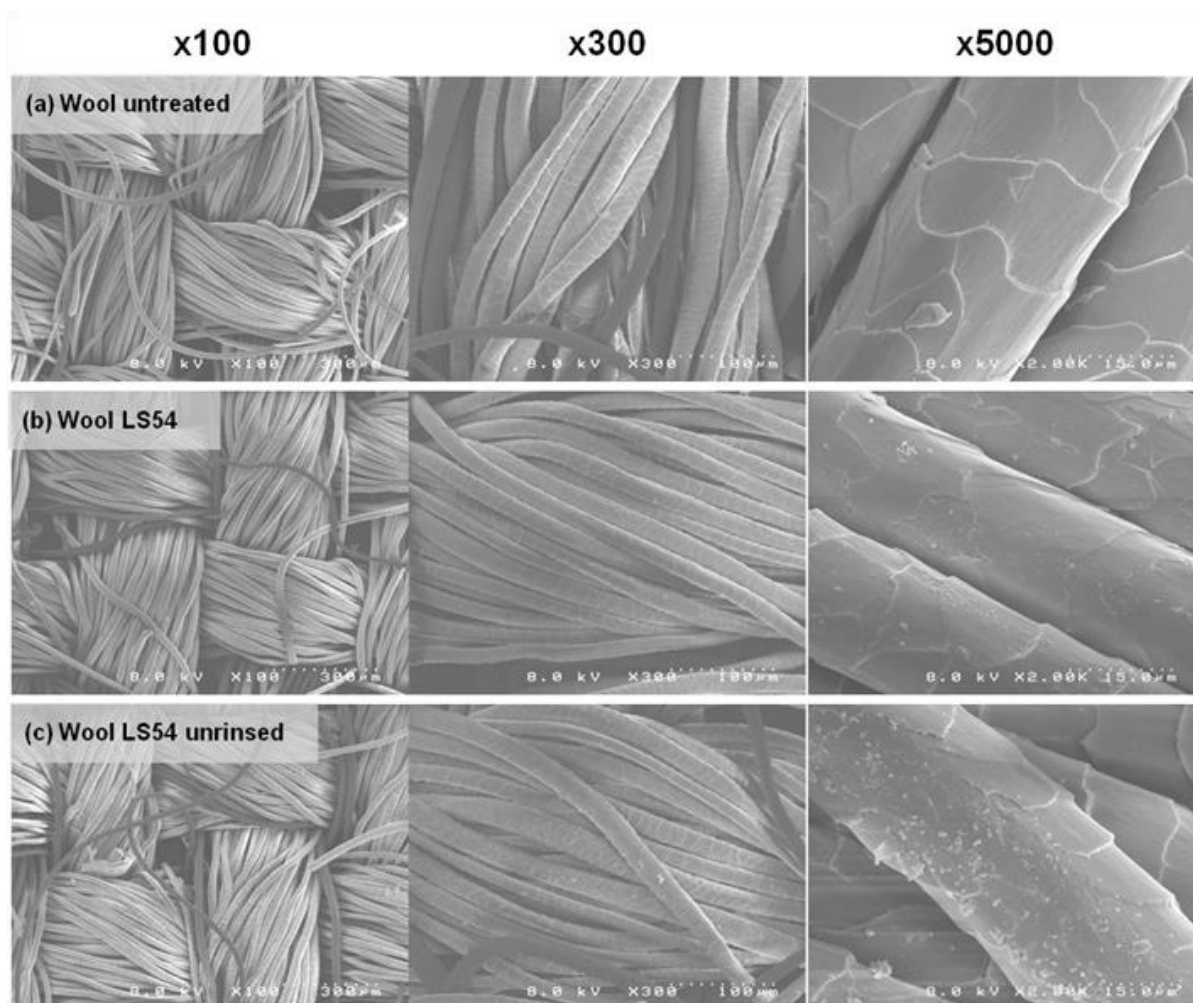
Fig. 5-29 SEM micrographs of wool surface before (a) and after washed by LS54 with (b) and without rinsing (c). The magnifications were ×100, ×500 and ×5000 (left to right).

5.5 Conclusion

To develop the analytical method to detect residue of Dehypon® LS45 and LS54 on cotton and wool, DRIFTs technique was used and any characteristic spectral differences relating to surfactant-fibre interaction were analysed. As there was a possibility of detecting surfactant residue on cotton and wool when they were not rinsed, this technique may be useful to know whether historical textiles, such as tapestry, have previously been washed by non-ionic fatty alcohol surfactants. A residue of LS45 and LS54 will not significantly affect thickness and tensile strength of fabrics. However, further testing is needed to observe physical properties between surfactants and fibres. From the DRIFTs analysis for neat solution, it was found that LS54 would be more hydrophilic and hence retain more water,

releasing it at a higher cloud point than LS45. It was also proved that LS45 would have a longer fatty alcohol chain, therefore its cmc is higher than LS54.

Chapter 6
Conclusion and Further Work

Non-ionic surfactant, Dehypon® LS45 (LS45), has been widely used for conservation wet cleaning in the UK. However LS45 has very low cloud point of 20 °C and it is hard to control temperature below the cloud point during wet cleaning. Therefore, it has been expected to find an alternative non-ionic surfactant. A prospective surfactant is Dehypon® LS54 (LS54; fatty alcohol C_{12-14} with 5 moles of ethylene oxide and 4 moles of propylene oxide), whose cloud point is 30 °C. It is currently used at the Victoria and Albert Museum as a trial while investigations into the chemical and physical structure of the surfactant itself and the effect of detergency on textiles are undertaken.

The aim of this research was to address the current problem of low cloud point of LS45, by evaluating LS54 as the alternative non-ionic surfactant. The research questions about LS54 were:

1. What is its cmc value, which is important for calculating how much to use?

2. How efficient is it at soil removal?

3. How efficient is rinsing for its removal to minimise residue on fibres?

The critical micelle concentration (cmc) is a property of a surfactant that is used to calculate its concentration in a wash bath. The cmc values of LS45 and LS54 were determined through surface tension measurements by the Wilhelmy plate method and compared to the

simplified drop weight method. In addition, in order to find out the optimum condition for wet cleaning with LS54, the detergency of artificially soiled cotton and wool was examined by comparison with LS45. Finally, there was a need to develop an analytical method to determine any residue on fabrics, Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs) was applied for detecting residue of LS45 and LS54 on unsoiled cotton and wool after washing treatment.

It was found that there is some confusion between the current and the supplier's cmc value of LS45 and LS54. Static surface tension was measured by the Wilhelmy plate method and dynamic surface tension was obtained by simplified drop weight method in order to determine cmc value of LS45 and LS54. This research has shown that the differences in cmc values between current cmc used by conservation and the supplier's cmc are due to the analytical method. Because the action of surfactants during wet cleaning is dependent on their interfacial dynamic surface tension, it was concluded that the apparent cmc value of LS54 would be best determined by dynamic surface tension measurements. The values obtained from experimentation using the Wilhelmy plate method ranged from 0.4 to 0.59 g/L. This experimental value corresponds to the tentative cmc 0.39 g/L calculated by V&A's methodology explained in Chapter 2. Furthermore, through the experiments, the cmc values of LS54 were found to be lower than that of LS45. This can reduce the amount of detergent for wet cleaning and has benefits for reducing the environmental impact of its use in conservation as well.

On the basis of the tentative and experimental cmc values, the most effective concentration of LS54 washing solution was tested. This was found to be 0.3% w/v (3 g/L) and the detergency effect was almost equal to LS45 at the same concentration. However, it should be noted that LS54 at 0.3% w/v is equal to ×7.5 cmc, based on the research in Chapters 2 and 3. Therefore, in order to achieve the same effect of detergency as LS45, LS54 would require slightly higher cmc value for washing while this has no affect on the amount of surfactants. It was also proved that LS54 was more effective at removing soils on cotton than LS45.

To investigate the possibility of detecting surfactant residue on cotton and wool when they were not rinsed well enough, a Diffuse Reflectance Infra Red Fourier Transform spectroscopy (DRIFTs) non-invasive analytical technique could applied for detecting residues was used. In addition, DRIFTs analysis proved that LS54 is more hydrophilic than LS45 and hence would retain more water, releasing it at a higher cloud point than LS45. It was also found that LS54 has a shorter fatty alcohol chain than LS45, so its cmc is lower than LS45.

The overall conclusion is that the non-ionic surfactant Dehypon® LS54 could be used as replacements for Dehypon® LS45 in conservation wet cleaning. However, further research is necessary not only to optimise the efficiency of soil removal, but also to evaluate its performance in real case studies to remove soiling from historical textiles.

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Accessed May 12, 2014.

Appendix 1: Materials and Suppliers

Unsoiled Fabrics

Cotton Lawn

    Whaleys (Bradford) Ltd.

    Harris Court, Great Horton, Bradford,

    West Yorkshire, BD7 4EQ, England

   http://www.whaleys-bradford.ltd.uk/
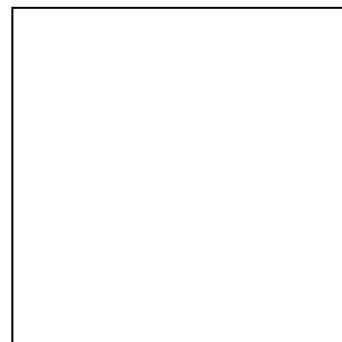
Wool Delaine Bleached (W11E)

    Whaleys (Bradford) Ltd.

    Harris Court, Great Horton, Bradford,

    West Yorkshire, BD7 4EQ, England

    http://www.whaleys-bradford.ltd.uk/
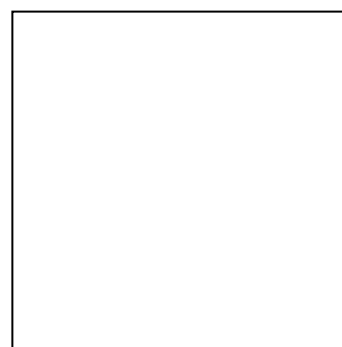
Soiled Fabrics

Cotton soiled with carbon black/olive oil (EMPA 101)

    Materials Research Products Ltd.

    Suite 236, 4 Montpelier Street, London,

    England SW7 1EX

    Tel: +44-20-7823-4146

    E-mail: info@mrpltd.com
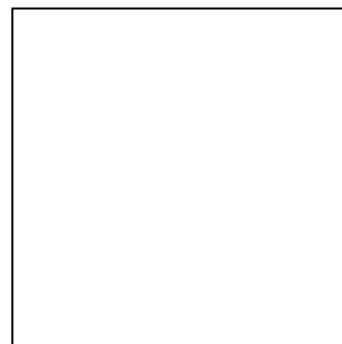
Wool soiled with carbon black/olive (EMPA 107)

    Materials Research Products Ltd.

    Suite 236, 4 Montpelier Street, London,

    England SW7 1EX

    Tel: +44-20-7823-4146

    E-mail: info@mrpltd.com
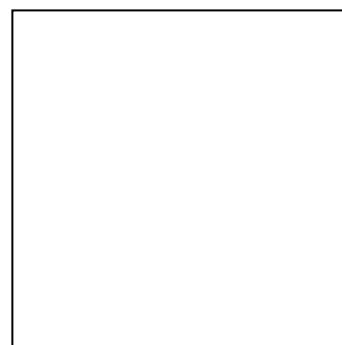
Surfactants

Dehypon® LS45

    Conservation By Design Ltd.

    Timecare Works, 5 Singer Way, Woburn Rd Ind. Estate,

    Kempston, Bedford, MK42 7AW, UK

    Tel: +44 1234 853555

    Web: http://www.conservation-by-design.co.uk

Dehypon® LS54

    BASF

    GUP/CI - LI554

    67117 Limburgerhof

    GERMANY

    Tel: +49 621 60-79134

    Web: http://www.basf.com/group/corporate/en/

Sponge

Ramer® sponge

    Boots UK Ltd.

    PO Box 5300, Nottingham, NG90 1AA

    Web: http://www.boots-uk.com/

Appendix 2: Concentration conversion table
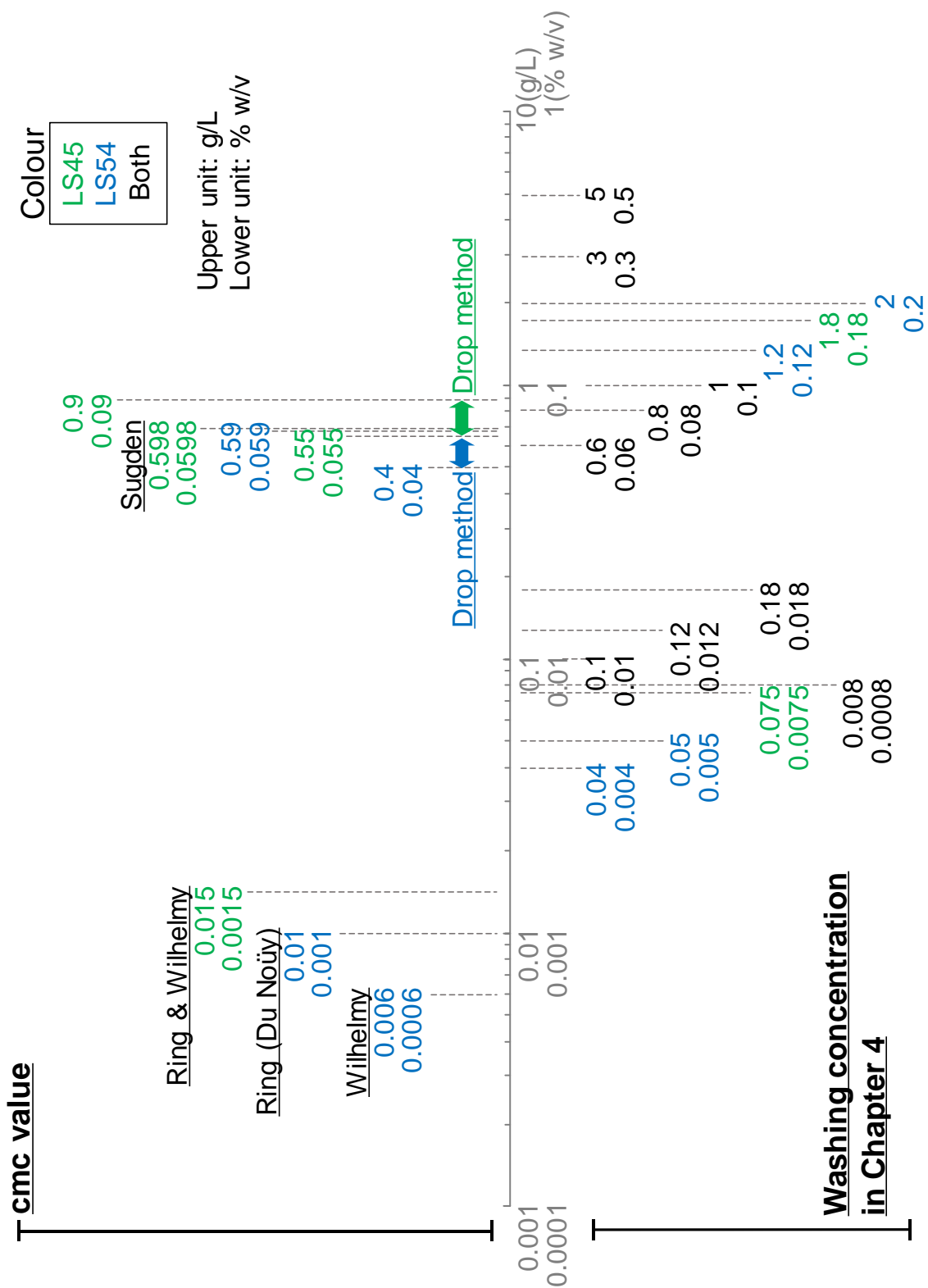
Appendix 3: Results of Chapter 4
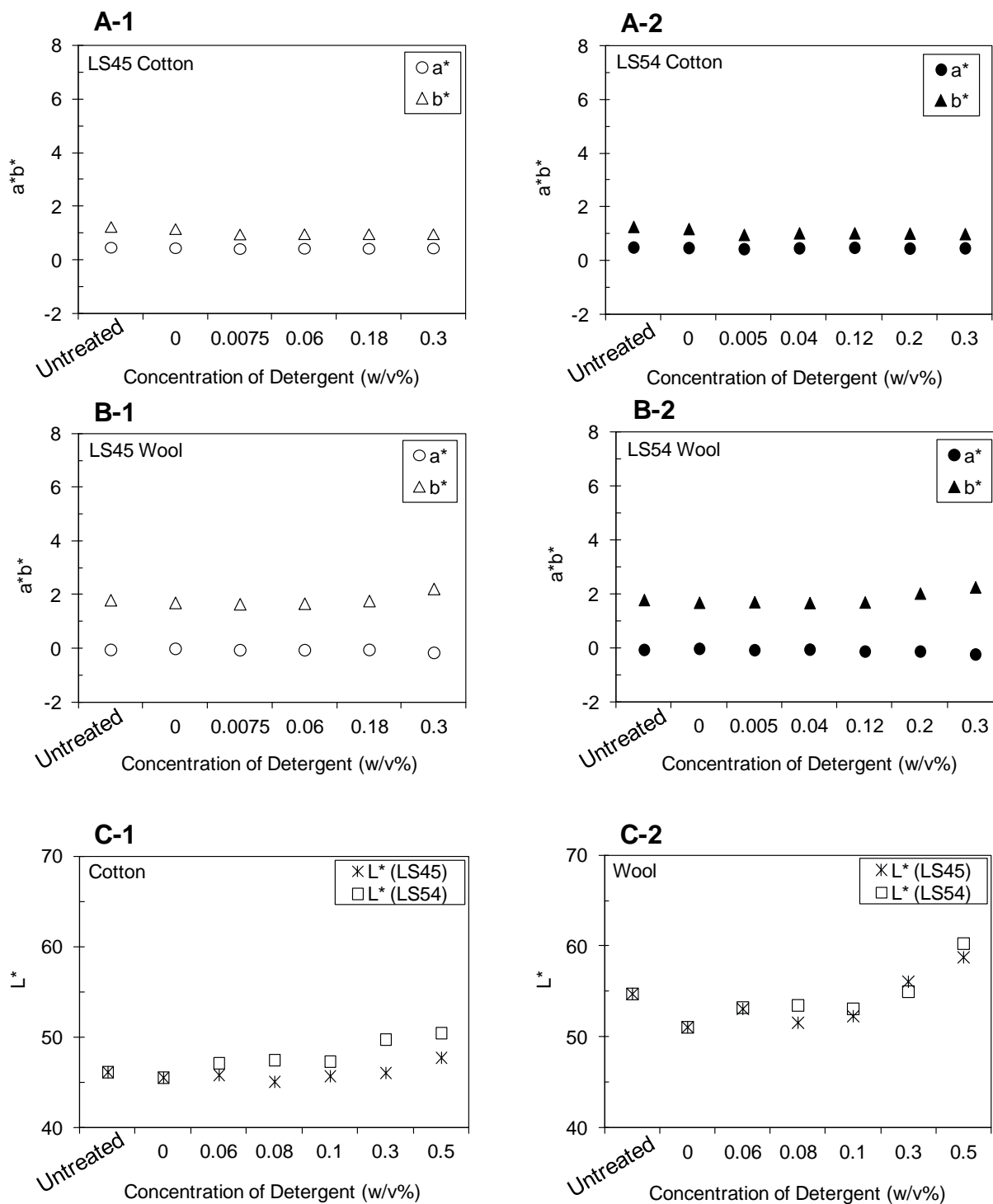
Fig. A3-1 Concentration-dependence of L*a*b* values showing before and after treatment.
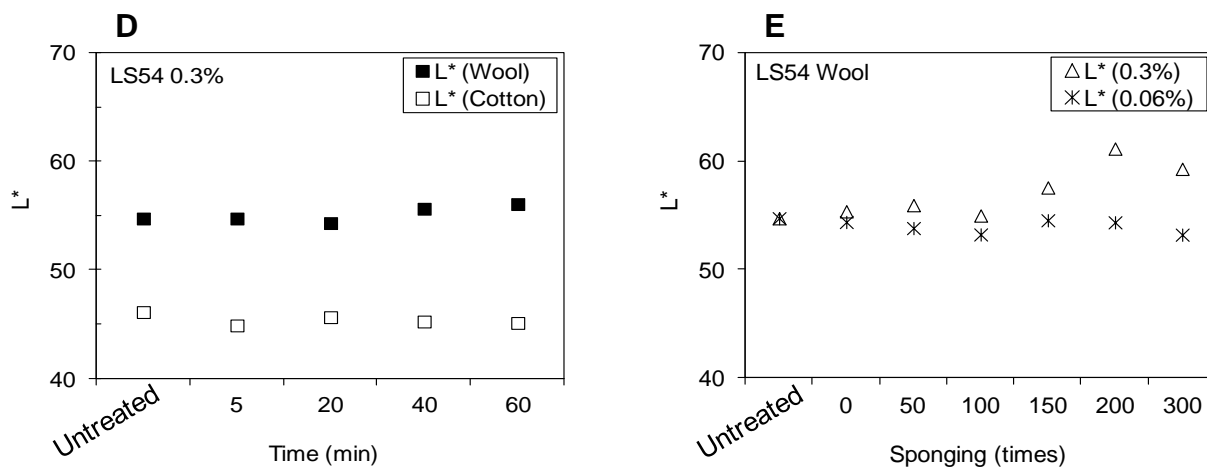
Fig. A3-2 Concentration-dependence of L* values showing before and after treatment.
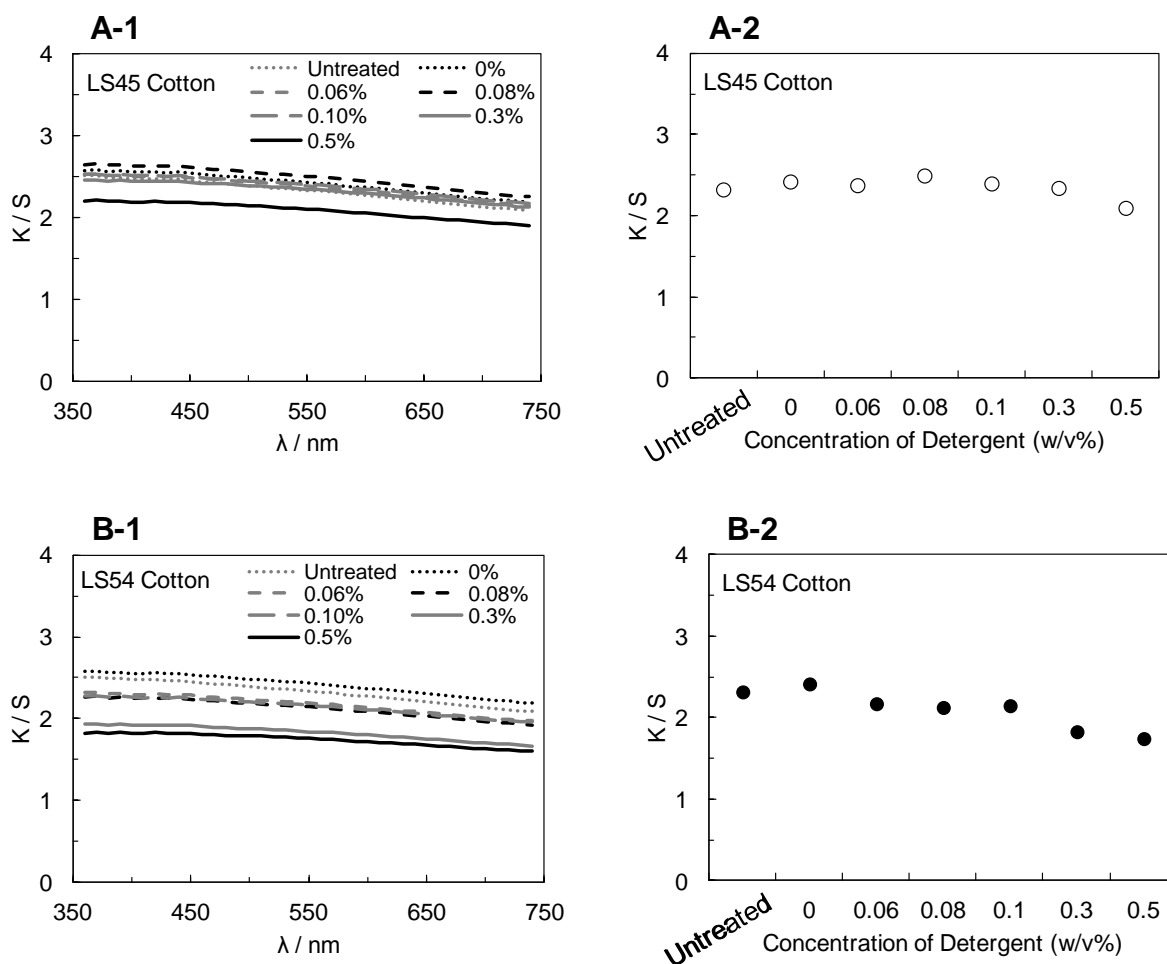
Fig. A3-3 The *K/S* spectrum (left) and concentration-dependence of *K/S* at 560 nm (right) of cotton washed by LS45 and LS54.
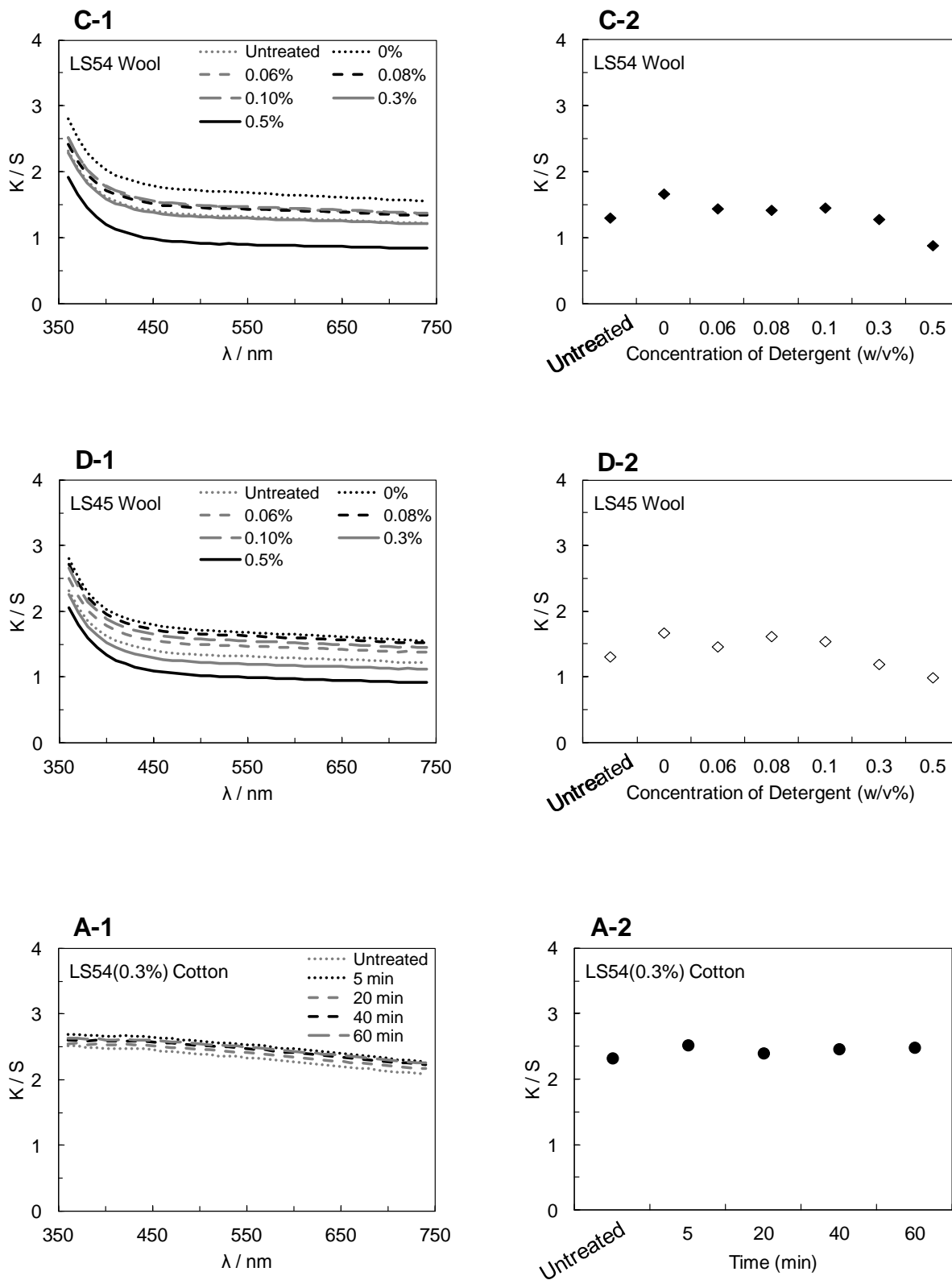
Fig. A3-4 The *K/S* spectrum (left) and concentration-dependence of *K/S* at 560 nm (right) of cotton washed by LS45 and LS54.
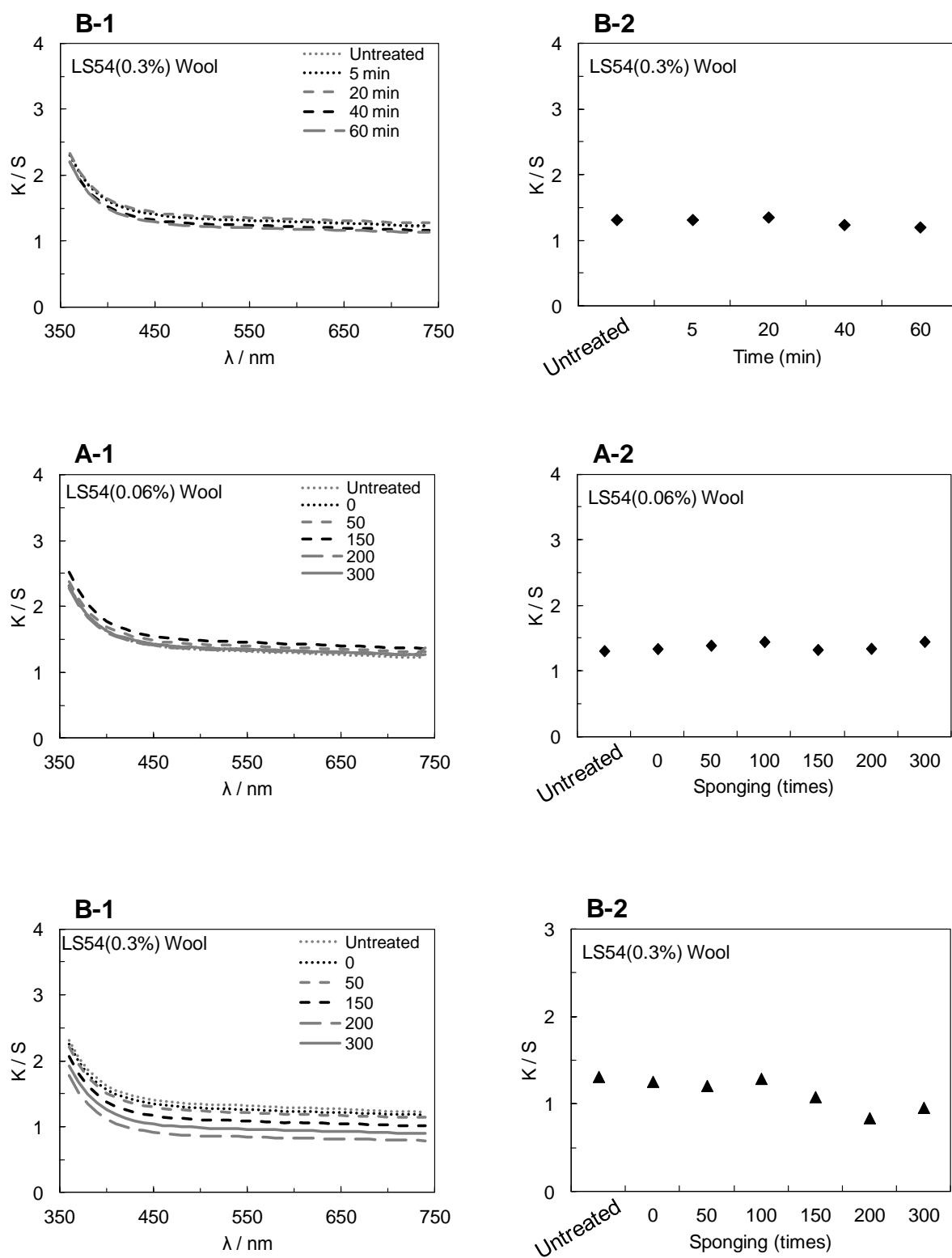
Fig. A3-5 The *K/S* spectrum (left) and concentration-dependence of *K/S* at 560 nm (right) of cotton washed by LS45 and LS54.

Appendix 4: Results of t-test

Table A4-1 Abbriviation of sample for t-test.

Sample ID	Fibre	Surfactant	Treatment
1	Cotton	N/A	N/A
2	Cotton	Water	N/A
3	Cotton	LS45	Rinsed
4	Cotton	LS45	Unrinsed
5	Cotton	LS54	Rinsed
6	Cotton	LS54	Unrinsed
7	Wool	Untreated	N/A
8	Wool	Water	N/A
9	Wool	LS45	Rinsed
10	Wool	LS45	Unrinsed
11	Wool	LS54	Rinsed
12	Wool	LS54	Unrinsed

Table A4-2 Cotton Break at Load

Test Round Pair		p value	$p =$
1	2	0.990014	NS
1	3	0.21281	NS
1	4	0.613163	NS
1	5	0.054947	NS
1	6	0.324958	NS
2	3	0.240983	NS
2	4	0.726353	NS
2	5	0.060928	NS
2	6	0.366937	NS
3	4	0.288423	NS
3	5	0.326983	NS
3	6	0.749726	NS
4	5	0.070339	NS
4	6	0.444333	NS
5	6	0.211402	NS

Table A4-3 Cotton Breaking Extension

Test Round Pair		p value	$p =$
1	2	0.237602	NS
1	3	0.629444	NS
1	4	0.066555	NS
1	5	0.356992	NS
1	6	0.006455	NS
2	3	0.184563	NS
2	4	0.652756	NS
2	5	0.151692	NS
2	6	0.001356	NS
3	4	0.094271	NS
3	5	0.564505	NS
3	6	0.072446	NS
4	5	0.111406	NS
4	6	0.00034	<0.001
5	6	0.452286	NS

Table A4-4 Wool Break at Load

Test Round Pair		p value	$p =$
7	8	0.632634	NS
7	9	0.186177	NS
7	10	0.496732	NS
7	11	0.816267	NS
7	12	0.321849	NS
8	9	0.08111	NS
8	10	0.256313	NS
8	11	0.566937	NS
8	12	0.581878	NS
9	10	0.501868	NS
9	11	0.489049	NS
9	12	0.037976	<0.05
10	11	0.801728	NS
10	12	0.114247	NS
11	12	0.34478	NS

Table A4-5 Wool Breaking Extension

Test Round Pair		p value	$p =$
7	8	0.036062	<0.05
7	9	0.036062	<0.05
7	10	0.000121	<0.001
7	11	0.070821	NS
7	12	0.002759	<0.01
8	9	0.550688	NS
8	10	0.005049	<0.05
8	11	0.984731	NS
8	12	0.05796	NS
9	10	0.000119	<0.001
9	11	0.624248	NS
9	12	0.023041	<0.05
10	11	0.018162	<0.05
10	12	0.444229	NS
11	12	0.089304	NS

Appendix 4: Results of t-test

Table A4-6 Abbriviation of sample for t-test.

Sample ID	Surfactant conc. (% w/v)	Treatment
A	N/A	N/A
B	0.3	Rinsed
C	0.3	Unrinsed
D	0.6	Rinsed
E	0.6	Unrinsed
F	0.9	Rinsed
G	0.9	Unrinsed
H	1.2	Rinsed
I	1.2	Unrinsed

C-LS45	Cotton	LS45
C-LS54	Cotton	LS54
W-LS45	Wool	LS45
W-LS54	Wool	LS54

Table A4-7 Cotton-LS45

Test Round Pair		p value	$p =$
A	B	0.000001	<0.001
A	C	0.000000	<0.001
A	D	0.000006	<0.001
A	E	0.000514	<0.001
A	F	0.452085	NS
A	G	0.015876	<0.05
A	H	0.106108	NS
A	I	0.000023	<0.001
B	C	0.552511	NS
B	D	0.046133	<0.05
B	E	0.001521	<0.01
B	F	0.000014	<0.001
B	G	0.000479	<0.001
B	H	0.000014	<0.001
B	I	0.065533	NS
C	D	0.104049	NS
C	E	0.002425	<0.01
C	F	0.000021	<0.001
C	G	0.000861	<0.001
C	H	0.000014	<0.001
C	I	0.143925	NS
D	E	0.067407	NS
D	F	0.000342	<0.001
D	G	0.016546	<0.05
D	H	0.000327	<0.001
D	I	1.000000	NS
E	F	0.012006	<0.05
E	G	0.342659	NS
E	H	0.025832	<0.05
E	I	0.099525	NS
F	G	0.113142	NS
F	H	0.497428	NS
F	I	0.000581	<0.001
G	H	0.264082	NS
G	I	0.024509	<0.05
H	I	0.000908	<0.001

Table A4-8 Cotton-LS54

Test Round Pair		p value	$p =$
A	B	0.000144	<0.001
A	C	0.004786	<0.01
A	D	0.000411	<0.001
A	E	0.000036	<0.001
A	F	0.000012	<0.001
A	G	0.000632	<0.001
A	H	0.001080	<0.01
A	I	0.000047	<0.001
B	C	0.227532	NS
B	D	0.501044	NS
B	E	0.821736	NS
B	F	0.613583	NS
B	G	0.425944	NS
B	H	0.325586	NS
B	I	0.059834	NS
C	D	0.525362	NS
C	E	0.245011	NS
C	F	0.083385	NS
C	G	0.613555	NS
C	H	0.753162	NS
C	I	0.009077	<0.01
D	E	0.580125	NS
D	F	0.206559	NS
D	G	0.888818	NS
D	H	0.729098	NS
D	I	0.020508	<0.05
E	F	0.387117	NS
E	G	0.484989	NS
E	H	0.359272	NS
E	I	0.034928	<0.05
F	G	0.167413	NS
F	H	0.116570	NS
F	I	0.098185	NS
G	H	0.837071	NS
G	I	0.016397	<0.05
H	I	0.012252	<0.05

Table Wool -LS45

Test Round Pair		p value	p =
A	B	0.012993	<0.05
A	C	0.653067	NS
A	D	0.10767	NS
A	E	0.602333	NS
A	F	0.905313	NS
A	G	0.163168	NS
A	H	0.546551	NS
A	I	0.036922	<0.05
B	C	0.087686	NS
B	D	0.001033	<0.05
B	E	0.032353	<0.05
B	F	0.066284	NS
B	G	0.002812	<0.05
B	H	0.01761	<0.05
B	I	0.000543	<0.001
C	D	0.132408	NS
C	E	0.444683	NS
C	F	0.803963	NS
C	G	0.136945	NS
C	H	0.39682	NS
C	I	0.040763	<0.05
D	E	0.710946	NS
D	F	0.26396	NS
D	G	0.736642	NS
D	H	0.666082	NS
D	I	0.269503	NS
E	F	0.601933	NS
E	G	0.583672	NS
E	H	1	NS
E	I	0.290844	NS
F	G	0.237519	NS
F	H	0.566695	NS
F	I	0.085904	NS
G	H	0.542192	NS
G	I	0.54286	NS
H	I	0.237494	NS

Table Wool-LS54

Test Round Pair		p value	p =
A	B	0.171463	NS
A	C	0.429936	NS
A	D	0.075579	NS
A	E	0.067404	NS
A	F	0.024766	<0.05
A	G	0.148257	NS
A	H	0.447068	NS
A	I	0.697393	NS
B	C	0.098305	NS
B	D	0.731829	NS
B	E	0.765875	NS
B	F	0.194965	NS
B	G	0.873117	NS
B	H	0.684607	NS
B	I	0.419894	NS
C	D	0.052525	NS
C	E	0.052285	NS
C	F	0.014986	<0.05
C	G	0.083893	NS
C	H	0.224804	NS
C	I	0.338844	NS
D	E	0.951082	NS
D	F	0.287305	NS
D	G	0.870264	NS
D	H	0.471377	NS
D	I	0.252738	NS
E	F	0.258326	NS
E	G	0.910088	NS
E	H	0.488755	NS
E	I	0.258331	NS
F	G	0.253292	NS
F	H	0.125592	NS
F	I	0.063185	NS
G	H	0.592086	NS
G	I	0.356241	NS
H	I	0.72804	NS

Appendix 5: Risk Assessment & COSHH Assessment Form

RISK ASSESSMENT FORM

University of Glasgow

School: Culture and Creative Arts	Section: Centre For Textile Conservation and Technical Art History	Location: Room number(s)309ab, 310,315	Reference No: R 5	/13-14	Related COSHH Form (if applicable):

Description of activity:

Dissertation research – measuring critical micelle concentration (cmc), wet cleaning and testing natural fibre test specimens by light ageing and tensile test

Persons at risk:
Students and tutors

Is operator training/supervision required? If yes, please specify:
Tutor will be present if supervision is required.

Hazards/ Risks	Current controls	Are these adequate?	What action is required if not adequately controlled?
Preparation of test specimens to include light ageing test – spills, breakage and burns	PPE (lab coat, gloves and heat proof gloves when using Xenon Test Chamber for ageing), clean up spills, dispose of any breakages correctly, maintain clear and clean workspace	Yes	
Measuring cmc and wet cleaning – slips, spills, breakages, using detergents	PPE (lab coat and gloves), clean up spills, dispose any breakages correctly, maintain clear and clean workspace and environment	No	Complete COSHH form for surfactants. See Dehypon® LS45 (C63 /13-14) and Dehypon® LS54 (C64 /13-14)
Glassware breakage	Dispose of broken glassware in glassware disposal container.	Yes	

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Electro equipment	Awareness of position of electrical cables to avoid risk of tripping.	Yes
Tensile strength test – injury to self when machine is running	Wear closed shoes, tie up hair and wear lab coat to prevent loose garments getting caught in the machine, take regular brakes to remain focused on task	Yes

Completed by (print name and position, and sign): 佐藤 萌 明
Moe Sato, student

Date:
20/5/2014

Approved by (print name and position, and sign): Karen Thorpe

Date:
21.5.14

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University of Glasgow

RISK ASSESSMENT FORM

School: Culture and Creative Arts	Section: Centre For Textile Conservation and Technical Art History	Location: Room number(s)_313_	Reference No: R 50/13-14	Related COSHH Form (if applicable): C___

Description of activity: Tensile testing using Instron 5544. This instrument uses up to a maximum load of 1000 newtons (1 kN) to measure the load and extension of a sample.

Persons at risk: U of G staff and students using equipment or present in room

Is operator training/supervision required? If yes, please specify: Yes. Work with member of staff who has experience of using the equipment. Two people need to be present when the instrument is being used.

Hazards/ Risks	Current controls	Are these adequate?	What action is required if not adequately controlled?
Trapping of limbs, hair, loose clothing, long accessories in jaws which exert high loads	Tie the hair back, remove any loose clothing and accessories. Keep hands etc well away from the equipment when it is exerting extension on a specimen. Good communication with others present when loading a sample – explain what you are planning to do.	Yes	
Use of foot pedal requires the user to kick a back plate to release the jaws of the instrument	Wear protective footwear. No open toed sandals or flip-flops.	Yes	

Completed by (print name and position, and sign):

Moe Sato, 佐藤 萌

Date: 03/09/2014

Approved by (print name and position, and sign):

Lorna Thompson

Date: 03/07/14

University of Glasgow

COSHH Assessment Form

School: Culture and Creative Arts
Section: Centre for Textile Conservation and Technical Art History
Project Title:

File ref: C63/13-14
Related Assessment Form: R 5/13-14
Date: 20/5/2014

Room Number(s): 309a+b, 310, 315

Building: Robertson Building, Level 3

Persons involved:

Students and staff

Description of procedure:

Making up surfactant solution from concentrate
Measuring critical micelle concentration
Aqueous cleaning with surfactant

Substance used	Quantities used	Frequency of use	Hazards identified	Exposure route
Dehypon® LS45 A low foaming nonionic surfactant with sufficient stability in alkaline media (e.g. carbonates, silicates, phosphates) and acidic media (e.g. phosphoric acid, critic acid).	>50 g	10-20 times from May to August in 2014	Eye/ skin irritation Ingestion	Skin contact Contact Ingestion

Could a less hazardous substance (or form of the substance) be used instead?   Yes/**no**

Justify not using it: Required for conservation treatment

What measures have you taken to control risk?

Engineering controls:

Eyewash facilities

Personal Protective Equipment:

Wear gloves, lab coat, apron, eyewear

Management measures:

Good workroom practice

Checks on control measures:

Tutor supervision

Is health surveillance required?	No	**Training requirements:** No

Emergency procedures: Eye contact: flush with water Skin irritation: flush with water Seek medical attention if ingested	**Waste disposal:** Do not empty into drains: Very toxic to aquatic organism

Name and position of assessor:
Moe Sato, Student

Signature: 佐藤 萌

Name of supervisor (student work only):
K. Thompson

Signature:

Name of Head of School or nominee:

Signature: Kara Thompson

University of Glasgow

COSHH Assessment Form

School: Culture and Creative Arts
Section: Centre for Textile Conservation and Technical Art History
Project Title:

File ref: C6f/13-14
Related Assessment Form: R 51/13-14
Date: 20/5/2014

Room Number(s): 309a+b, 310, 315	**Persons involved:**
Building: Robertson Building, Level 3	Students and staff

Description of procedure:

Making up surfactant solution from concentrate
Measuring critical micelle concentration
Aqueous cleaning with surfactant

Substance used	Quantities used	Frequency of use	Hazards identified	Exposure route
Dehypon® LS54 A low foaming nonionic surfactant. C12-14, ethoxylated propoxylated	>50 g	10-20 times from May to August in 2014	Eye/ skin irritation Ingestion	Skin contact Contact Ingestion

Could a less hazardous substance (or form of the substance) be used instead? Yes/**no**

Justify not using it: Required for conservation treatment

What measures have you taken to control risk?

Engineering controls:

Eyewash facilities

Personal Protective Equipment:

Wear gloves, lab coat, apron, eyewear

Management measures:

Good workroom practice

Checks on control measures:

Tutor supervision

Is health surveillance required? No	**Training requirements:** No

Emergency procedures:	**Waste disposal:**
Inhaled: Keep patient calm, remove to fresh air Skin irritation: Wash thoroughly with soap and water Eye contact: flush with water Ingestion: Rinse mouth immediately and then drink plenty of water, induce vomiting, seek medical attention	Do not empty into drains: Very toxic to aquatic organism

Name and position of assessor:
Moe Sato, Student

Signature: 佐藤 萌

Name of supervisor (student work only):
K. Thompson

Signature: Karen Thompson

Name of Head of School or nominee:

Signature: