

# Role of Polyoxyethylene Ethers Nonionic Surfactants in Leather Dyeing: Investigation by Spectrophotometry and Dynamic Light Scattering Method

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**Abstract:** The interactions among polyoxyethylene ethers nonionic surfactants ( $C_{18}POE_n$ ), C.I. Direct black 19 and gelatin were studied by spectrophotometry. Combining reflectance measurements, the effect of  $C_{18}POE_n$  and its adding order on leather dyeing kinetics and surface color were analyzed. Moreover, particle sizes in  $C_{18}POE_n$  solutions with C.I. Direct black 19 or gelatin were estimated by dynamic light scattering method. There were complexes formed by hydrogen bonds and hydrophobic interactions among  $C_{18}POE_n$ , C.I. Direct black 19 and gelatin. With  $C_{18}POE_n$  the dyeing process was slowed down; the uniformity and shade of surface color were improved. Furthermore,  $C_{18}POE_n$  added together with dye can bring the best levelling effect. Particle size results suggest that  $C_{18}POE_n$  is prone to interact with dye, not with gelatin. All these results verify that the levelling effect of polyoxyethylene ethers nonionic surfactants depend on the interactions between surfactants and dyes. The study shall facilitate the use of advanced analytic techniques for understanding leather dyeing process.

**Key words :** leather, dyeing, polyoxyethylene ethers nonionic surfactants, spectrophotometry, dynamic light scattering method

## 1 Introduction

As estimated, 50-60% of all leather is dyed black. In leather industry the color black is as popular as ever and it is set to continue to be in great demand in the future. Among all kinds of dyestuffs, acid black and direct black dyestuffs dominate in the leather dyeing process. Direct black dyestuffs are easy to colorize leather surface and cover the damages, but difficult to dye through the whole cross section of leather. Therefore some nonionic surfactants (such as the polyoxyethylene ethers nonionic ones) are added as levelling or dispersing agents in leather dyeing process.

Although several researches have been done on dye-surfactant interactions by using spectrophotometry, potentiometry and surface tension measurements et al.<sup>[1-4]</sup>, there are scarce recoveries on the use of such advanced techniques for studying leather dyeing process. In this study, C.I. Direct black 19 as an example, the absorbance spectrograms of the mixtures of polyoxyethylene octadecyl alcohol ether ( $C_{18}POE_n$ ,  $n=15$  or  $16$ ), the dye and gelatin were measured to speculate on their interactions. Meanwhile, the effect of adding order of  $C_{18}POE_n$  on the dyeing kinetics and the surface color of dyed leathers were analyzed by spectrophotometry and reflectance measurements. In the end, the interactions between  $C_{18}POE_n$  and gelatin or C.I. Direct black 19 were estimated by dynamic light scattering method.

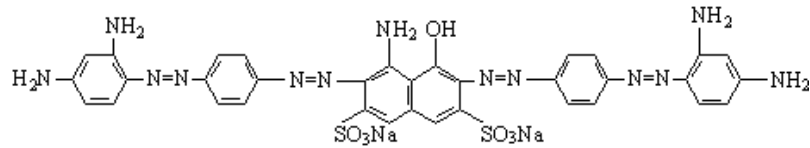
## 2 Experimental

### 2.1 Materials

$C_{18}POE_n$  ( $n=15$  or  $16$ ) was supplied by Shangyu Printing and Dyeing Assistants Co.(China) with 99% purity. C.I. Direct black 19(Fig. 1) was supplied by Tianjin Dyestuff Chemistry Co. (China) with 100% strength. Gelatin (biochemical reagent) was purchased from Sigma-Aldrich Co.(USA). All the

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reagents were used as received. Water used in the preparation of the solutions for spectrophotometric and dynamic light scattering measurements was deionized twice.



**Fig.1 Structure of C.I. Direct black 19**

## 2.2 Methods

### 2.2.1 CMC measurements

The surface tension of aqueous solutions of the nonionic surfactant ( $C_{18}POE_n$ ) at various concentrations was measured by using Pendant drop method with Dataphysics OCA H200 Contact Angle Analyser (Germany). The Critical Micelle Concentration (CMC) value was determined at sharp break points in surface tension against the logarithm of the concentration curve. The CMC value was found to be 0.05% for  $C_{18}POE_n$  at 25 °C. From the surface tension measurement, the CMC value of  $C_{18}POE_n$  did not vary within the temperature range of 25-50 °C. Therefore, it was selected from a wide concentration range.

### 2.2.2 Preparation of the dye, surfactant and gelatin solutions

Considering the CMC value for  $C_{18}POE_n$  as 0.05%, the mixtures of C.I. Direct black 19 and  $C_{18}POE_n$  were prepared as 5:5, 5:4, 5:3 and 5:2 parts by mass, and the dye concentration was set as 0.1%. Similarly, the mixed solutions of gelatin, C.I. Direct black 19 and  $C_{18}POE_n$  were prepared as 10:1:0.8, 10:1:1 and 10:1:1.2 parts by mass, and the dye concentration was set as 0.05%.

### 2.2.3 Spectrophotometric measurements

The prepared solutions were shaken in a thermostat bath at 40 °C for 60min. Then the spectrophotometric measurements were done by using Lambda 25 UV-vis spectrophotometer (PerkinElmer Instruments Co., USA.) with a thermostat controller at 40 °C. The absorbance spectrogram was recorded between 400nm and 800nm.

### 2.2.4 Dyeing

Conventional chrome tanned bovine leather was selected for the study. The leather was sammed and shaved to 1.70-1.80mm thickness and then cut into 20×25cm size samples. Prior to dyeing, all the samples were rechromed and neutralized to pH about 5.5. Next, every two of them were taken for each trial and processed in the drum as per process described in Tab. 1. Quantity of chemicals was calculated on shaved weight.

**Tab. 1 Dyeing recipe of bovine leather**

Samples	Chemicals	T ( °C )	Time ( min )	Check
Control	100% water	40	20	pH 3.5 ± 0.1
	2.5% C.I. Direct Black 19		80	
	1%formic acid		30	
Trial 1	100% water	40	20	pH 3.5 ± 0.1
	0.2% $C_{18}POE_n$		80	
	2.5% C.I. Direct Black 19		30	
Trial 2	1% formic acid	40	30	pH 3.5 ± 0.1
	100% water		20	

	0.2% C <sub>18</sub> POE <sub>n</sub>			
	2.5% C.I. Direct Black 19		80	
	1% formic acid		30	pH 3.5 ± 0.1
Trial 3	100% water	40	20	
	2.5% C.I. Direct Black 19		20	
	0.2% C <sub>18</sub> POE <sub>n</sub>		60	
	1% formic acid		30	pH 3.5 ± 0.1

The sample leathers were rinsed in water for 10min and then dried in the air.

### 2.2.5 Analysis of dye exhaustion in the process liquor

Exhausted dye liquor was collected every 10min and analyzed for unspent dye using spectrophotometric method by measuring the absorbance value at the  $\lambda_{max}$  of the dye, after suitably diluting the spent dyeing liquor. The amount of dye present in the spent liquor was calculated from the calibration graph drawn for the known concentration of the dye. Then the dye exhaustion was calculated using equation (1).

$$\text{Dye exhaustion}(\%) = \frac{C_u - C_r}{C_u} \times 100\% \quad (1)$$

Here,  $C_u$  is the concentration of dye used,  $C_r$  is the concentration of dye present in the spent liquor.

### 2.2.6 Determination of surface color difference

The control and experimental leathers were subjected to the reflectance measurements using a X-riteColor Premier8200 (X-Rite Co., USA.). Color measurements ( $L$ ,  $a$ ,  $b$  and  $c$ ) were recorded. Wherein ' $a$ ' represents the red and green axes and ' $b$ ' represents the yellow and blue axes. The total color difference ( $\Delta E$ ) was calculated using equation (2).

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (2)$$

$\Delta L < 0$ , sample is darker,  $\Delta L > 0$ , sample is lighter;

$\Delta a < 0$ , sample is greener,  $\Delta a > 0$ , sample is redder;

$\Delta b < 0$ , sample is bluer,  $\Delta b > 0$ , sample is more yellow;

$\Delta c < 0$ , sample is brighter/more saturated,  $\Delta c > 0$ , sample is duller/less saturated.

### 2.2.7 Determination of fastness to wet/dry rub

The control and experimental leathers were conditioned at  $20 \pm 1^\circ\text{C}$  and  $65 \pm 2\%$  relative humidity for 72hours<sup>[5]</sup>. Next, the color fastness to to and fro rubbing was tested according to ISO 11640:1993<sup>[6]</sup> and assessed according to the standard staining grey scales.

### 2.2.8 Determination of the size distribution of particles

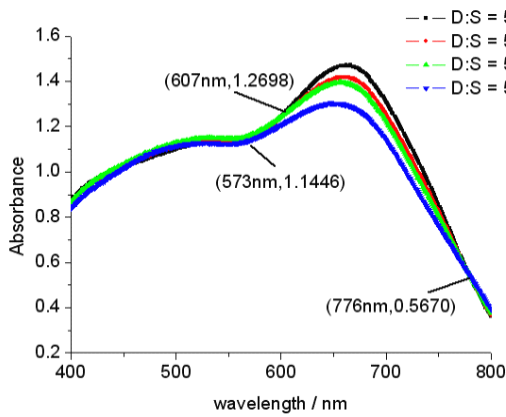
0.5% C.I. Direct black 19, 0.5% gelatin and 0.5% C<sub>18</sub>POE<sub>n</sub> solutions were prepared respectively. Meanwhile, the mixtures of C<sub>18</sub>POE<sub>n</sub> and dye / gelatin were prepared as 1:10 parts by mass. The size distributions of particles in the above solutions were analyzed by using a Zetasizer Nano ZS instrument (Malvern Instruments Co., UK) at  $25^\circ\text{C}$ .

## 3 Results and discussions

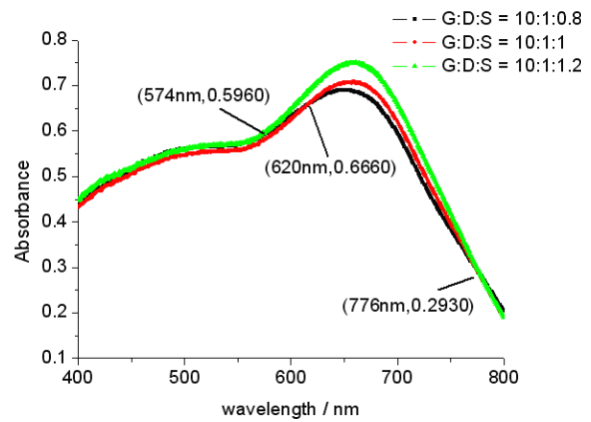
### 3.1 Spectrophotometric measurements

The presence of several isosbestic points indicates the existence of several species (soluble / insoluble

ones) at equilibrium, which has been verified by other researchers [7-10]. As soluble complex is formed from insoluble one, the hydrophobic interactions must be involved [8,11-16].



**Fig. 2 Absorption spectrograms of mixtures of C.I. Direct Black 19 (D) and C<sub>18</sub>POE<sub>n</sub> (S) (C.I. Direct Black 19 concentration was set as 0.1% in the four mixtures)**

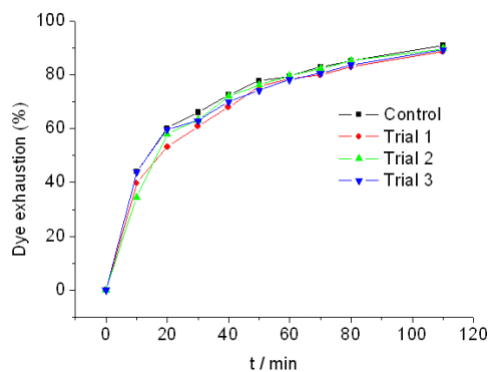


**Fig. 3 Absorption spectrograms of mixtures of C.I. Direct Black 19 (D), C<sub>18</sub>POE<sub>n</sub> (S) and Gelatin (G) (C.I. Direct Black 19 concentration was set as 0.05% in the three mixtures)**

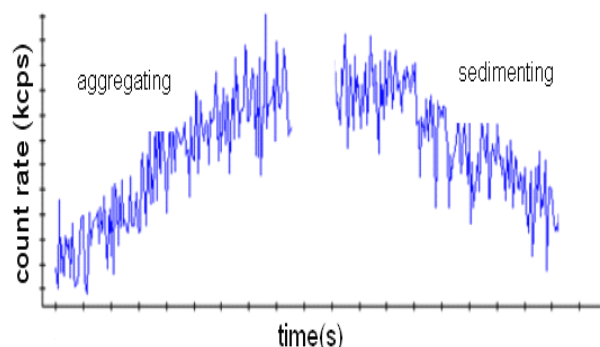
Fig. 2 shows bathochromic shift and the increase of the absorbance between 573nm and 776nm with increasing C<sub>18</sub>POE<sub>n</sub> concentration. There are three isosbestic points (573nm, 607nm and 776nm) which may indicate the formation of soluble / insoluble dye-surfactant complexes. As a result, there should be hydrophobic interactions between dye and C<sub>18</sub>POE<sub>n</sub>. When C<sub>18</sub>POE<sub>n</sub> concentration is higher than its CMC value(0.05%), the absorbance between 574nm and 776nm of the mixtures of C.I. Direct black 19, C<sub>18</sub>POE<sub>n</sub> and gelatin increases greatly(Fig. 3). Similar to Fig. 2, three isosbestic points (574 nm, 620nm and 776 nm) may suggest the formation of the insoluble / soluble complexes and the existence of hydrophobic interactions between C<sub>18</sub>POE<sub>n</sub> and C.I. Direct black 19 or gelatin. Furthermore, all these spectrograms reveal that the interactions between dye and surfactants can evidently alter the absorbance between 573nm and 700nm, this will change the color of the mixed solutions and may influence the color of dyed leathers.

### 3.2 Dyeing kinetics

Fig. 4 shows the dyeing kinetics of bovine leather with C.I. Direct black 19. When C<sub>18</sub>POE<sub>n</sub> added in different orders, the final dye exhaustion varied little, but the dye exhaustion had some decrease in early 60min. Particularly the dye exhaustion in Trial 2 was slower and more even than that in Trial 1 and Trial 3. Since C.I. Direct black 19 can interact to C<sub>18</sub>POE<sub>n</sub> more effectively (see Fig. 2), C<sub>18</sub>POE<sub>n</sub> added together with the dye can bring about the best levelling effect. C<sub>18</sub>POE<sub>n</sub> can slow down the dyeing process, which should be the main reason for the levelling effect of C<sub>18</sub>POE<sub>n</sub>.



**Fig. 4 Dye exhaustion (%) at 40°C**



**Fig. 5 Count rate for aggregating/sedimenting samples**

### 3.3 Surface color

By visual assessment, the uniformity and shade of surface color and dye penetration are better for the experimental samples. From the  $\Delta L$  and  $\Delta c$  values shown in Tab. 2, there is a decrease in the darkness and an increase in the intensity in the presence of  $C_{18}POE_n$ . Compared to the controls, the surface color of dyed leathers in three Trials are redder. The total color difference ( $\Delta E$ ) varies little with  $C_{18}POE_n$  added in different orders. These results are consistent with the influence of  $C_{18}POE_n$  on the absorbance spectrogram of C.I. Direct black 19 (bathochromic shift).

**Tab. 2 Color difference values of control and experimental leathers**

Samples	$\Delta L$	$\Delta a$	$\Delta b$	$\Delta c$	$\Delta E$
Control <sup>a</sup>	16.55	0.26	0.19	0.32	0
Trial 1	0.82	0.19	0.34	0.38	0.97
Trial 2	0.72	0.23	0.49	0.52	0.92
Trial 3	0.55	0.29	0.58	0.63	0.87

<sup>a</sup> The values in the first row were the color measurements ( $L, a, b$  and  $c$ ) for the control.

### 3.4 Rub fastness characteristics of leathers

The rub fastness of controls and experimental samples are shown in Tab. 3. The experimental samples have similar fastness to the controls. This indicates that there is little effect of  $C_{18}POE_n$  on the rub fastness of surface color of dyed leathers.

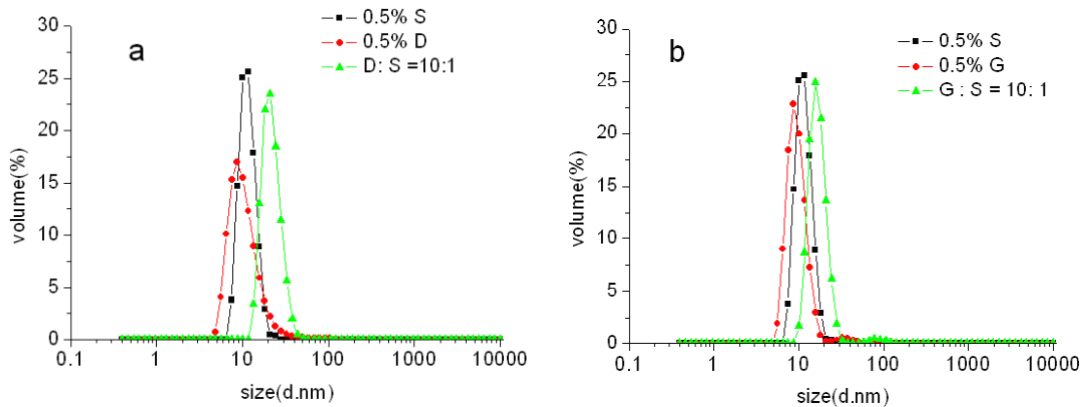
**Tab. 3 Rub fastness of controls and experimental samples**

Samples	Rub fastness	
	Dry rub (25 times)	Wet rub (20 times)
Control	3~4	3
Trial 1	3~4	3
Trial 2	3~4	3
Trial 3	3~4	3

### 3.5 Size distribution of particles in $C_{18}POE_n$ and dye/gelatin solutions

Quasi-elastic light scattering is related to the moving of particles in macromolecular solutions, and the hydromechanical radius of macromolecules can be determined by using dynamic light scattering

method. With concentrations higher than the CMC value, the surfactant molecules will tend to form micelles of sizes between 5nm and 100nm<sup>[17-19]</sup>. So the particle size distribution can be estimated by the dynamic light scattering method. According to the ‘Zetasizer Nano User Manual’<sup>[20]</sup>, during the size measurement process, the steady increasing or decreasing count rate is correlated to the aggregating or sedimenting samples(Fig. 5).



**Fig. 6** Particles size distributions in  $C_{18}POE_n$ (S), C.I. Direct Black 19(D) and gelatin(G) solutions

During the size measurement process for the mixtures of  $C_{18}POE_n$  and gelatin/dye, the change tendency of the count rate was found to be similar to that in Fig. 5. This denominates that gelatin/dye may have some interactions with  $C_{18}POE_n$  and form several species. Fig. 6 indicates that there is an increase in the sizes of particles in the  $C_{18}POE_n$  solutions with gelatin or dye, and the dye can bring larger rise to the particle sizes. This means that the interactions of  $C_{18}POE_n$  with the dye should be stronger than that with gelatin. That is, the levelling effect of  $C_{18}POE_n$  should depend more on the interactions with the dye molecules.

### 3.6 Plausible levelling effect mechanism of $C_{18}POE_n$

Collagen, as the main component of leather, contains acidic amino acid, basic amino acid and a relatively high percentage of proline and hydroproline. The nonionic surfactant  $C_{18}POE_n$  has ‘O’ in ethylene oxide, which can interact to ‘H’ in C.I. Direct black 19 and amino acid groups of collagen by hydrogen bonds in leather dyeing process. This has been verified by the variation of the absorbance band and bathochromic shift in Fig. 2 and Fig. 3. In addition, the existence of isosbestic points in absorbance spectrograms suggests that there are hydrophobic interactions among C.I. Direct black 19,  $C_{18}POE_n$  and gelatin. As a result, the corresponding soluble / insoluble complexes were formed by the two interactions. The increase of particle sizes in  $C_{18}POE_n$  solutions with C.I. Direct black 19 are larger than that with gelatin, indicating that  $C_{18}POE_n$  are tend to interact with dye molecules. The increase in the sizes of dye- $C_{18}POE_n$  complexes can help to slow down the diffusion and penetration of the dye, and colorize the leather surface to obtain more uniform surface color. All these results verify that the levelling effect of polyoxyethylene ethers nonionic surfactants should depend more on the interactions between surfactants and dyes.

## 4 Conclusions

The spectrophotometry results indicate there are soluble / insoluble complexes formed by hydrogen bonds and hydrophobic interactions among  $C_{18}POE_n$ , C.I. Direct black 19 and gelatin.

In the presence of  $C_{18}POE_n$ , the absorbance spectrograms of C.I. Direct black 19 (or with gelatin)

solutions show evident bathochromic shift; the leather dyeing process was slowed down; the uniformity of surface color and dye penetration were improved; the shade of surface color was redder; but the rub fastness varied little. In addition,  $C_{18}POE_n$  added together with the dye can bring about the optimum levelling effect.

Sizes of particles in  $C_{18}POE_n$  solutions got larger with dye than with gelatin. The levelling effect of polyoxyethylene ethers nonionic surfactants depends more on the interactions between surfactants and dyes.

## Acknowledgements

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## References

- [1] Y. Jiang, Interaction of surfactants and aminoindophenol dye, *Journal of Colloid and Interface Science*, 2004, 274(1): 237 -243.
- [2] Navarro A, Cegarra J, Valldeperas J, Influence of oxyethylenated alkylamines in the dyeing of polyamide 66 fibres, *Dyes and Pigments*, 2006, 69(1-2): 40-44.
- [3] Simončič B, Kert M., Influence of the chemical structure of dyes and surfactants on their interactions in binary and ternary mixture, *Dyes and Pigments*, 2008,76(1):104-112.
- [4] Kert M, Simončič B., The influence of nonionic surfactant structure on the thermodynamics of anionic dye-cationic surfactant interactions in ternary mixtures, *Dyes and Pigments*, 2008,79(1):59-68.
- [5] W. Q. Jiang, *Physical and Chemical Inspection of Leather*, Light Industry Publishing Company, Beijing,2004,17.
- [6] ISO 11640-1993: International Organization for Standardization(1993),Color fastness of leather to rubbing.
- [7] Hughes JA, Sumner HH, I-A study of the mechanisms, *Journal of the Society of Dyers and Colourists*, 1971,87(12): 463 -472.
- [8] Cegarra J, Valldeperas J, Navarro JA, Influence of Oxyethylenated Alkylamines in the Dyeing of Wool, *Journal of the Society of Dyers and Colourists*, 1983,99(10): 291- 296.
- [9] Nemoto Y, Funahashi H., The Interaction between Dyes and Nonionic Surfactants: the Mode of Action on Nonionic Surfactants in Dyeing, *Industrial and Engineering Chemistry Research*,1980,19(6):136-142.
- [10] Stevenson DM, Duff DG, Kirkwood DJ, The behaviour of dyes in aqueous solutions. Part II-anionic dye-nonionic surfactant interactions, *Journal of the Society of Dyers and Colourists*, 1981,97(1):13-17.
- [11] Tsatsaroni EG, Eleftheriadis IC, Kehayoglou AH, The role of polyoxyethylenated stearylamine in the dyeing of cotton with direct dyes, *Journal of the Society of Dyers and Colourists*, 1990,106(7/8): 245-248.
- [12] Simončič B, Span J, A study of dye-surfactant interactions. Part 1. Effect of chemical structure of acid dyes and surfactants on the complex formation, *Dyes and Pigments*, 1998,36(1):1-14.
- [13] Simončič B, Kovac F, A study of dye-surfactant interactions. Part 2. The effect of purity of a commercial cationic dye on dye-surfactant complex formation, *Dyes and Pigments*,1998,40(1):1-9.
- [14] Forte Tavcer P, Span J, Dye-Surfactant Interactions Studied Using Job's Method, *Journal of Textile Research*, 1999,69:278-284.
- [15] Simončič B, Span J, A study of dye-surfactant interactions. Part 3. Thermodynamics of the association of C.I. Acid Orange 7 and cetylpyridinium chloride in aqueous solutions, *Dyes and Pigments*, 2000,46(1):1-8.
- [16] Forte Tavcer P, Interactions between some anionic dyes and cationic surfactants with different alkyl chain length studied by the method of continuous variations, *Dyes and Pigments*, 2004,63:181- 189.
- [17] Cazabat A.M., Langevin D, *Light Scattering in Liquids and Macromolecular solutions*, Degiorgio V., Corti M.

and Giglio M. (eds.), Plenum Press, New York, 1980,139.

- [18] Candau F., Leong Y.S., Pouyet G., Inverse microemulsion polymerization of acrylamide-characterization of the water-in-oil microemulsions and the final microlatexes, *Journal of Colloid and Interface Science*, 1984,101:167-183.
- [19] Cazabat A.M., *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*, Degiorgio V. and Corti M. (eds.), North-Holland, Amsterdam, 1985,723.
- [20] Malvern Instrument, Co., *Zetasizer Nano Series User Manual*, MAN 0317, Issue 2.2, England, March 2005.

### **Appendix:**

Although the collagen in crust leather for dyeing are often crosslinked by some tanning agents(such as, chromitan, vegetable tannins, et al.), the stabilized collagen has the same conformation as that of native collagen.(See in the article: Nishtar Nishad Fathima, Raju Suresh, Jonnalagadda Raghava Rao, et al., Effect of UV irradiation on stabilized collagen: Role of chromium (III),*Colloids and Surfaces B: Biointerfaces*,2008,62:11-16.) As you know, gelatin is a hydrolysate from collagen. So, the stabilized collagen and gelatin are still homologous, and they may have analogous physicochemical characteristics. As a result, the behavior of gelatin towards the dye can be used to mimic that of the tanned hide with the dye.