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Electrokinetic Study of Water Hardness during Acid Dyeing with Silk

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Abstract
In this paper, the effect of water hardness, expressed in $CaCO_3$, on the dyeing of silk with acid dye under acid, alkaline and isoelectric point dyeing conditions was studied using the zeta potential method. Under acidic conditions and in the presence of calcium ion, the positive zeta potential of silk was found to decrease with a reduction in dye adsorption. Such a phenomenon might be due to the presence of cation which increased the dyeing potential barrier at the interface between fibre and dye solution. This would result in a higher resistance of dye anions passing through the interface. Under alkaline conditions the zeta potential of silk was negative and resulted in a strong potential barrier against the dye anions. The presence of calcium ions would result in a decrease in the absolute value of the zeta potential of silk fibre, with an overall increase in dye absorption. At the isoelectric point, the zeta potential of the silk fibre was found to be near zero, and the dye adsorption was not influenced by the cations. These results showed that calcium ions could have a strong electrolytic effect on dyeing, even at very low concentrations.

Key words: *water hardness, silk, acid dye, zeta potential.*

Introduction

In the textile dyeing process, water quality plays an important role in determining the final shades of the products. One of the important factors in governing the dyehouse water quality is the hardness, which is defined as the presence of soluble calcium and magnesium salts in the water and is expressed as the $CaCO_3$ equivalent. The presence of hardness in the water can cause dye precipitation, and the precipitates can further promote dye aggregations, which results in colour specks and loss of depth. Although the influence of hardness on dyeing has been widely investigated [1 - 7], there has been little discussion regarding silk [8, 9]. Thus, this paper deals with the electrolytic effect, especially on the electrokinetic properties of the dyeing process.

Electrokinetic phenomena are concerned with the transport of electric charge in porous media under the influence of an electric field and pressure gradient. The study of zeta potential is one of the techniques for studying electrokinetic phenomena in the wet processing of textiles. The adsorption of dyes alters the values of the zeta potential of fibres and the conditions of the dyeing process, i.e. temperature, electrolyte addition, dyeing auxilaries, etc. In this paper, the zeta potential method was used for determining the effect of hardness on the adsorption of acid dye by silk fibre under acid, alkaline and isoelectric point dyeing conditions using calcium ions within the range of 0 to 600 ppm.

Experimental

Materials

Water hardness was prepared by adding anhydrous $CaSO_4$ (A. R. Grade) to double-deionised water and then titrated against a standard EDTA solution of 0.01 molar concentration. The total water harness was expressed as $CaCO_3$ equivalent, ppm [10]. C.I. Acid Red 1 was used in this study and was purified by the method of DMF dissolution-acetone precipitation [11, 12]. Scoured pure silk crepe satin was used throughout this study.

Measurement of Zeta potential

The zeta potential was measured by a Zeta potential analyser (Beckman Coulter, Delsa 440sx). A 0.1 g/l acid dye solution was employed throughout all experiments, in which silk samples weighing 0.4 grams were soaked in different concentrations of hardness solutions for 24 hours at 25 ± 1 °C. The zeta potential (ζ) was calculated by using the Helmholtz-Smoluchwski equation [13 - 16].

Results and discussion

Determination of the isoelectric point (IEP) of silk

Figure 1 (see page 100) shows the zeta potential of silk fibres when immersed in 0.01 M (HCl + KCl) ionic strength solutions under different pH conditions. We can state on the basis of ***Figure 1*** that in this study the IEP of the silk fibres is pH 3.8.

Zeta potential of silk fibres dyed under acidic conditions

The zeta potential values of the silk fibres in both pure $CaSO_4$ solutions and $CaSO_4$ plus dye solutions under acidic condition, i.e. pH = 2.5, are plotted in ***Figure 2*** (see page 100) as a function of the $CaSO_4$ concentration. All zeta potentials are positive but show a declining value under the influence of an increased amount of

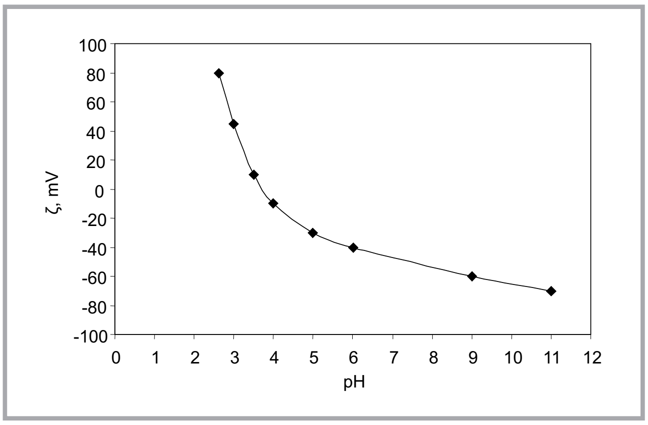

***Figure 1.** Zeta potential vs. of pH for silk of 0.01M ionic strength.*

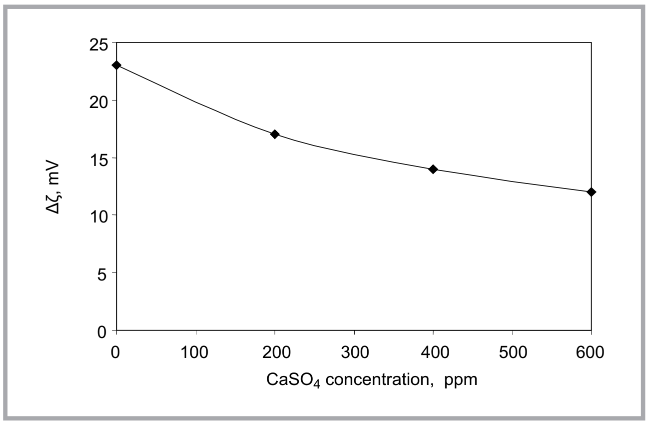

***Figure 3.** Relationship between Δζ and $CaSO_4$ concentrations.*

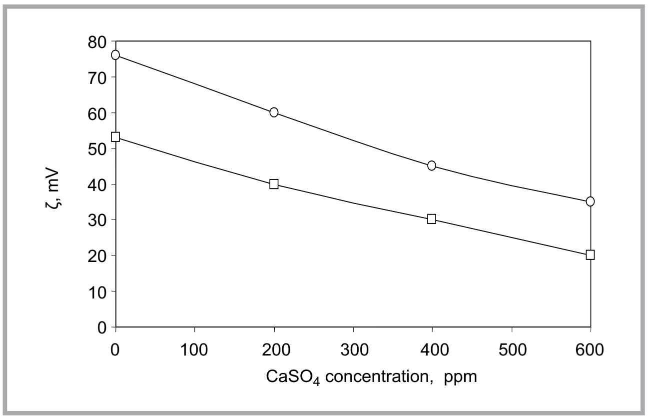

***Figure 2.** Relationship between the zeta potential and $CaSO_4$ concentration under acidic conditions (○ – $CaSO_4$ solution only, □ – $CaSO_4$ + dye solution).*

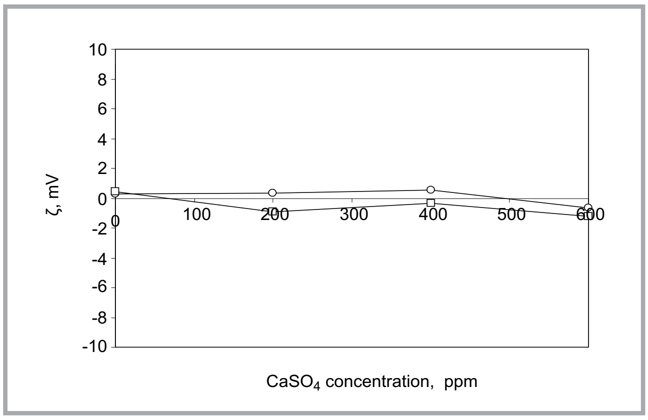

***Figure 4.** Relationship between the zeta potential and $CaSO_4$ concentration at IEP (○ – $CaSO_4$ solution only, □ – $CaSO_4$ + dye solution).*

$CaSO_4$. This result can be explained by the fact that the SO_4^{2-} anions dissociated from $CaSO_4$ were absorbed by the positive charges of the surface at the interface between the silk fibre and solution.

With acid dye added to the $CaSO_4$ solutions, there was a marked decrease in the zeta potential because of the shielding effect of the dye molecules which carry the negatively charged SO_3^- groups. ***Figure 3*** shows the values of

$$\Delta\zeta = \zeta_{CaSO4} - \zeta_{dye + CaSO4}$$

as a function of the $CaSO_4$ concentration. The values of Δζ can be used for expressing the ability or affinity of silk to absorb dye anions – the larger the Δζ values, the higher the affinity. ***Figure 2*** clearly indicates that under acid condition, dye anions are easily adsorbed by silk fibres, which is because of their positive charge and the strong affinity between dye anions and silk fibre. However, ***Figure 3*** shows that with increased $CaSO_4$ concentration, there was a gradual decrease in the Δζ. This result clearly indicated that under acid dyeing condition, the presence of salt could reduce the value of Δζ. Such a reduction would mean a reduction in dye affinity and result in a lower dye uptake.

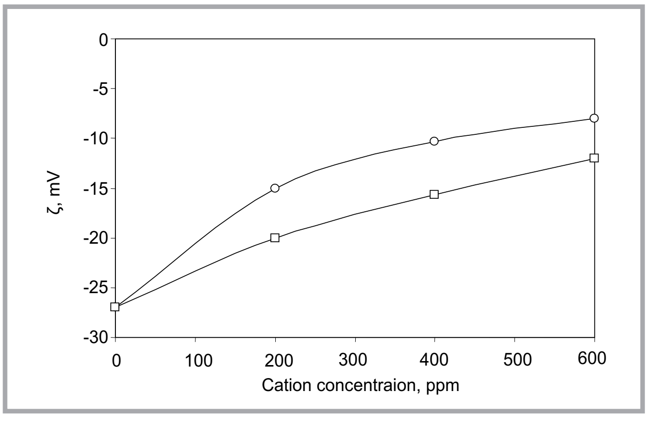

***Figure 5.** Relationship between the zeta potential of silk and the concentration of Ca^{2+} (○) and Na^+ (□) under alkaline conditions.*

Zeta potential of silk fibres dyed at IEP

The zeta potential values of the silk fibres in $CaSO_4$ solutions and $CaSO_4$ plus dye solutions at the IEP of silk (pH = 3.8) were plotted in ***Figure 4*** as a function of $CaSO_4$ concentration. It shows that the zeta potential of silk was only slightly influenced by the cation, with a value around zero irrespective of the amount of cation and dye present. Therefore, it can be concluded that the influence of calcium ions on dye exhaustion at IEP was not significant.

Zeta potential of silk fibres dyed under alkaline conditions

Figure 5 shows the variation of the zeta potential of silk with different concentrations of cations under alkaline conditions, i.e. pH = 10. Sodium ions were included in this study for comparison purposes. Under such conditions, silk carried negative charges and the zeta potential on its surface was also found to be negative. The negative charges cause a strong potential barrier to dye anions. The larger the value of |ζ| , the stronger the repulsion force or the potential barrier to dyeing between silk and dye anions would be.

The presence of cations in the dye solutions sharply reduces the |ζ| of silk. ***Figure 5*** shows that under the influence of Ca^{2+}, the |ζ| of the silk decreased markedly from 0 to 300 ppm; but such as decrease became less pronounced with a higher concentration of cations. For Na^{+}, the |ζ| decreased, in quite a linear manner, from 0 to 600 ppm. The decrease in |ζ| is due to the strong attraction force between the cations and the negatively charged surface of silk; these cations could partially screen the fibre-water interface of silk by crowding the cations. Such crowding could neutralise the negative charges of silk and reduce the repulsive forces between silk and dye anions. As a result, there is an increase in the chemical potential of dyeing, which in turn leads to increased dye exhaustion.

The extent of adsorption of cations on the surface of silk , or the ability of cations to contribute to the charge of |ζ|, is closely related to the properties of cations. Since the charge density of calcium is higher than that of sodium, their overall screening effect was also found to be stronger. At low concentrations the screening effect plays an important role, in which calcium ions could reduce |ζ| to a greater extent. However, when the concentration of cation is high, the ability to modify the fibre-water interface plays a decisive role [17]. Since the ability of calcium ions to modify the fibre-water interface is smaller than that of sodium ions, the rate of the decrease in |ζ| under the influence of calcium ions became less pronounced with higher concentrations.

Conclusions

The influence of water hardness on silk dyeing with acid dye, with the use of calcium ions, can be divided into three kinds according to the property of silk. Under acidic conditions, with the presence of calcium ions, the positive zeta potential of silk was found to decrease, and the dye adsorption also decreased. Such a phenomenon could be due to the presence of cations in the dyebath, which increased the dyeing potential barrier at the interface between fibre and dye solution. As a result, there was a higher resistance of dye anions passing through the interface. Under alkaline conditions, the zeta potential of silk was negative and resulted in a strong barrier to the dye anions. The presence of calcium ions would result in an overall decrease in the absolute value of the zeta potential of silk fibre, with a resultant increase in dye. At IEP the cations had little effect on the zeta potential of the silk fibre, which was found to be around zero, and the dye adsorption had also not been influenced. These results showed that calcium ions are able to produce strong electrolytic effects on dyeing even at very low concentrations. Because the screening ability of the sodium ion was smaller than that of the calcium ion, when the concentration was low, the overall reduction in absolute values of the zeta potential due to sodium ions was found to be smaller.

References

1. *Huo M., Baughman G. L.; Dyes and Pigments, 1992, 18: pp. 35-46.*
2. *Weible K. H.; Melliand Textilberichte, 1990, 71(10): E361-E362.*
3. *Jain A. K., Metha K. S.; ATIRA Communication on Textiles, 1991, 25(4): pp. 105-111.*
4. *Sampath M. R.; Colourage, 2001, 48(6): pp. 73-76.*
5. *Chapatwala M. N., Kapadia, P. J., Gandhi, R. S.; Colourage, 1994, 41(4): pp. 29-41.*
6. *Ishtiaque S. M., Parmar, M. S., Chakraborty, M.; Colourage, 2000, 47(9): pp. 15-24.*
7. *Rai I.; Colourage, 1996, 43(2): pp. 24-26.*
8. *Iyer N. D.; Colourage, 2005, 52(7): pp. 65-66.*
9. *Pathak S., Prabhu J., Somasekhar T. H.; Indian Journal of Fibre and Textile Research, 1996, 21(12): pp. 283-285.*
10. *Easter E., Lietzke M. H.; Textile Chemists and Colorists, 1982, 14(4): pp. 89-90.*
11. *Metha H.U., Ravikrishnan M.R., Chitale, A. G., Journal of Society of Dyers and Colourists, 1962, 78: pp. 552-559.*
12. *Hall D. M., Perkins W. S., Textile Research Journal, 1971, 41: pp. 923-927.*
13. *Capablanca J. S., Watt I. C., Textile Research Journal, 1986, 56: pp. 49-55.*
14. *Carrion F. J., Journal of Society of Dyers and Colourists, 1987, 103: pp.359-364.*
15. *Kale P. D., Lokhande H.T., Journal of Applied Polymer Science, 1975, 19: pp. 461-480.*
16. *Lokhande H. T., Salvi A. S., Colloid and Polymer Science, 1976, 254: pp. 1030-1041.*
17. *Madan G. L., Shrivastava S. K., Textile Research Journal, 1979, 49: pp. 322-325.*

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