EFFECT OF WATER HARDNESS ON ACID DYEING WITH SILK

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Abstract:

In this paper, the effect of water hardness, expressed in CaCO3 equivalent, on the dyeing of silk with acid dye under acid, alkaline and isoelectric point dyeing conditions was studied by the zeta potential method. Under acid conditions and in the presence of the calcium ion, the positive zeta potential of silk was found to decrease with a reduction in the dye adsorption. Such a phenomenon might be due to the presence of cation, which increases the dyeing potential barrier at the interface between the fibre and dye solution. This would result in a higher resistance of dye anions passing through the interface. Under alkaline conditions, the zeta potential on silk was negative and resulted in a strong potential barrier for the dye anions. The presence of the calcium ion would result in a decrease in the absolute value of zeta potential of silk fibre, with an overall increase in dye absorption. Under the isoelectric point, the zeta potential of silk fibre was found to be near zero and dye adsorption was not influenced by the cations. These results demonstrate that the calcium ion could produce a strong electrolytic effect on dyeing, even under very low concentrations.

Keywords:

fiber, surfaces, 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 influencing the dyehouse water quality is its hardness, which is defined as the presence of soluble calcium and magnesium salts in the water and expressed in the form of $CaCO_3$ equivalent. The presence of hardness in water can cause dye precipitation and the precipitates can further promote dye aggregations, which result in colour specks and loss of depth. Although the influence of hardness on dyeing has been widely investigated [1-3], this paper deals with the electrolytic effect, especially on the electrokinetic properties in the dyeing process.

Electrokinetic phenomena are concerned with the transport of electric charges in porous media under the influence of an electric field and pressure gradient. The assessment 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, using calcium ions, in the range of 0 to 600 ppm, on the adsorption of acid dye on silk fibre under acid, alkaline and isoelectric point dyeing conditions.

Experimental Data

Materials

Water hardness was prepared by adding anhydrous $CaSO_4$ (A.R. Grade) to double-deionised water and titrated against standard EDTA solution of 0.01 molar concentration. The total water hardness was expressed as $CaCO_3$ equivalent, ppm [4]. C.I. Acid Red 1 was used in this study and was purified by the DMF dissolution-acetone precipitation method [5,6]. Scoured pure silk crepe satin was used throughout this study.

Zeta potential measurement

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 and the silk samples, consisting of 0.4 grams, were soaked in solutions with differing concentrations of hardness for 24 hours at 25±1şC. The zeta potential (z) was calculated using the Helmholtz-Smoluchwski equation [7-10].

Results and Discussion

Determination of the isoelectric point (IEP) of silk

Figure 1 shows the zeta potential of silk fibres when immersed in 0.01M (HCl + KCl) ionic strength solutions under different pH conditions. Since IEP is defined as the pH value under which z = 0, it can be observed from Figure 1 that the IEP of the silk fibre is pH 3.8 in this study.

Zeta potential of silk fibres dyed at acidic condition

The zeta potential values of the silk fibres in both pure $CaSO_4$ solutions and $CaSO_4$ plus dye solutions at acidic condition, i.e. pH = 2.5, are plotted in Figure 2 as a function of $CaSO_4$ concentration. All zeta potentials are positive, but they show a declining value under the influence of increased amounts of $CaSO_4$. This result can be explained on the basis that the anions of SO_4^{2-} dissociated from $CaSO_4$ were absorbed by the positive charges of the surface at the interface between the silk fibre and solution.

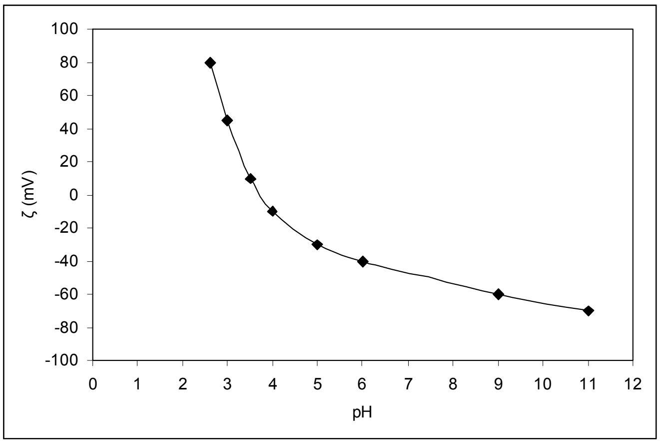

Figure 1. Zeta potential as a function of pH for silk at 0.01M ionic strength.

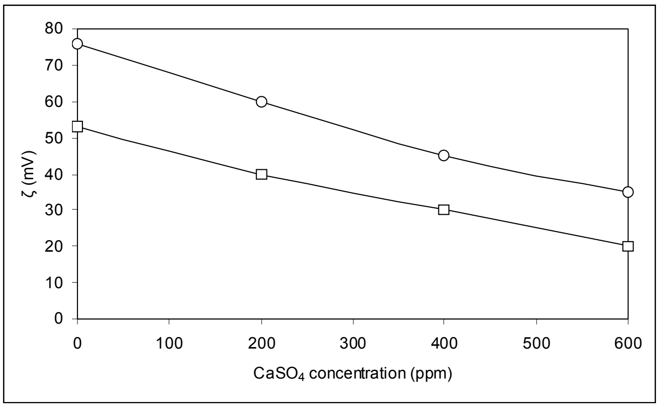

Figure 2. The relationship between zeta potential and $CaSO_4$ concentration under acidic condition (% – $CaSO_4$ solution only, % – $CaSO_4$ + dye solution).

When acid dye was 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_4^{2-} groups. Figure 3 shows the values of = $Dz_{CaSO4} - Dz_{dye + CaSO4}$, as a function of $CaSO_4$ concentration. The values of Dz could be used for expressing the adsorption ability or affinity of silk for dye anions – the larger the Dz values, the higher the affinity. From Figure 2, it can be clearly observed that under acid condition, dye anions are easily adsorbed by the silk fibres because they carry a positive charge and there is a strong affinity between dye anions and silk fibre. However, Figure 3 shows that with an increased $CaSO_4$ concentration, there is a gradual decrease in the Dz. This result clearly indicates that under acid dyeing condition, the presence of salt can reduce the value of Dz. Such a reduction would mean a reduction in dye affinity and result in a lower dye uptake.

Zeta potential of silk fibres dyed at IEP

The zeta potential values of 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. The graph shows that the zeta potential of silk is 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 the calcium ion on dye exhaustion at IEP is not significant.

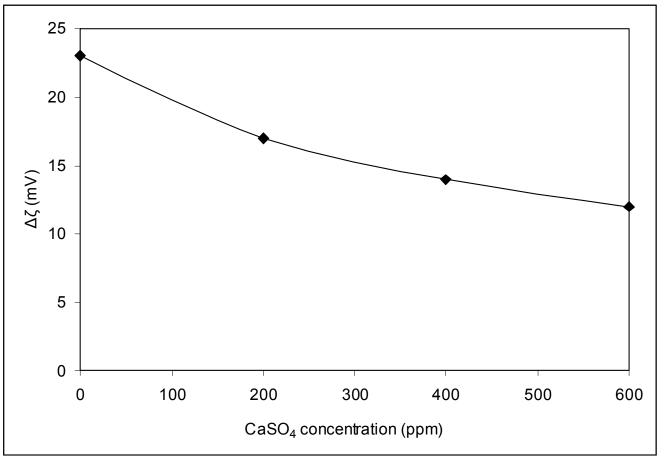

Figure 3. The relationship between and $CaSO_4$ concentration.

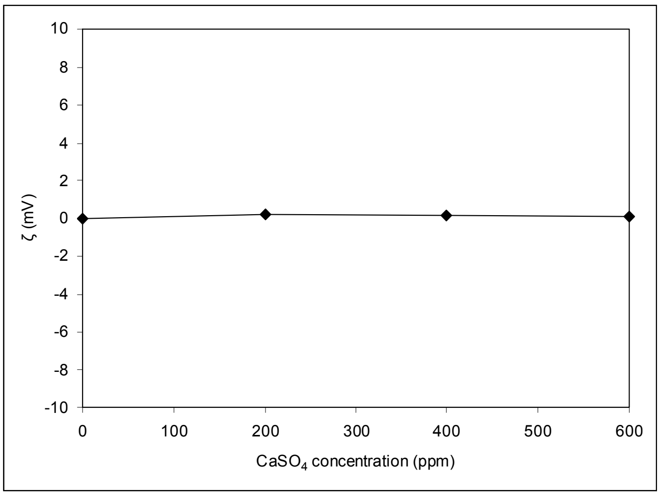

Figure 4. The relationship between zeta potential and $CaSO_4$ concentration at IEP.

Zeta potential of silk fibres dyed at alkaline condition

Figure 5 shows the variation of zeta potential of silk with different concentrations of cations at alkaline condition, 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 for dye anions. The larger the value of |z|, the stronger would be the repulsion force, or the potential barrier for dyeing, between silk and dye anions.

The presence of cations in the dye solutions sharply reduces the |z| of silk. Figure 5 shows that under the influence of Ca^{2+}, the |ζ| of silk decreased markedly from 0 to 300 ppm, but that the decrease became less pronounced with a higher concentration of cations. For Na^+, the |z| decreased in quite a linear manner from 0 to 600 ppm. The decrease of |z| 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 silk surface, or the ability of cations to contribute to the charge of |z|, 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 and calcium ions can reduce the |z| to a greater extent. However, when the concentration of cation is high, the ability to modify the fibre-water interface plays a decisive role [11]. Since the ability of the calcium ion to modify the fibre-water interface is smaller than that of the sodium ion, as a result the rate of the decrease in |z| under the influence of the calcium ion becomes less pronounced with higher concentrations.

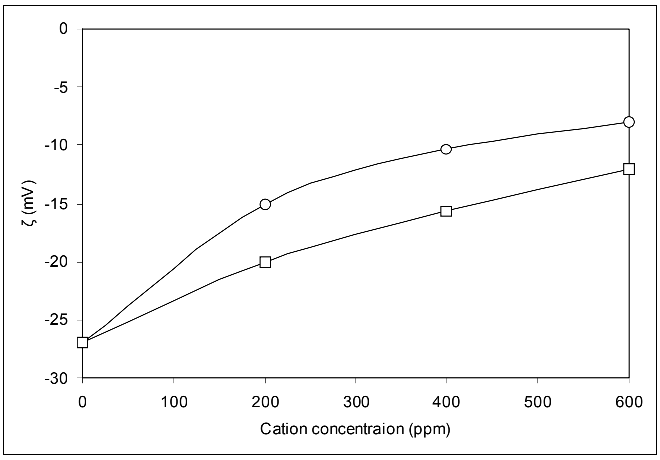

Figure 5. The relationship between the zeta potential of silk and the concentration of Ca^{2+} (%) and Na^{+} (%) under alkaline condition.

Conclusion

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

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