SOLVENT DYEING OF COTTON WITH ANIONIC DYES

by
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Dedicated

to

my parents

CERTIFICATE

This is to certify that the thesis entitled "SOLVENT DYEING OF COTTON WITH ANIONIC DYES", submitted by Mr. J. Venkata Rao to the Indian Institute of Technology Delhi, for the award of degree of DOCTOR OF PHILOSOPHY is a record of the bonafied research work carried out by him. Mr. J. Venkata Rao has worked under my guidance for the submission of this thesis, which to my knowledge has reached the requisite standard.

The thesis or any part thereof, has not been submitted to any other University or Institution for the award of any Degree or Diploma.

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ABSTRACT

An attempt was made to understand the dyeing mechanism of water swollen-sovent exchanged (WSSE) cotton with anionic dyes from dimethylformamide-trichloroethylene (DMF-TCE) solvent mixtures. For this purpose three anionic dyes, Naphthalene Red JS (CI Acid Red 88), Naphthalene Red EA (CI Acid Red 13) and Naphthalene Scarlet 4R (CI Acid Red 18) having the same structure but varying number of sulphonic acid groups from 1 to 3 were selected. The dyeing of WSSE cotton with anionic dyes was explained on the basis of the electrokinetic character of cotton in the solvent medium, analysis of adsorption isotherms, dyeing behaviour of oxidized cotton and the use of solubility parameter concept. The state of dye in solution was determined from the aggregation behaviour of the dyes in DMF-TCE solvent mixtures using a new technique, namely, quasielastic light scattering.

SYNOPSIS

Water as a medium for chemical processing of textiles is used universally. However, its use is not free from problems such as effluent treatment, stream pollution and high thermal energy required for evaporation. The use of non-aqueous medium was therefore considered to be an alternative medium for chemical processing of textiles. Chlorinated hydrocarbons such as perchloroethylene, trichloroethylene, 1,1,1-trichloroethane etc., were found to be more suitable for this purpose on the basis of their non-inflammability, stability towards repeated recovery and low thermal energy required for evaporation. Processes such as scouring of natural and synthetic fibres have been commercialised using these solvents. Considerable information is also available on the dyeing of synthetic fibres such as polyester with disperse dyes. This was possible because of non ionic nature of the dyeing system. However dyeing of natural fibres such as cotton with anionic dyes using chlorinated hydrocarbons was not possible due to non-polar nature of the solvents the fibre swelling was poor and the anionic dyes were insoluble in such solvents. To overcome these problems, it was essential to use a polar solvent

like water or dimethyl formamide (DMF) at certain stage of dyeing for fibre swelling and dye solubilization. Certain systems have been reported in the literature based on the above principle [1-4,7]. A more systematic study has been reported by Chavan and Co-workers for the dyeing of cotton with acid, direct and reactive dyes using polar and non-polar solvent mixtures [13-17]. It was reported that a reactive dye could successfully be exhausted and fixed on cotton when the dyeing was carried out from dimethyl formamide-trichloroethylene (DMF-TCE) solvent mixture. This study is of importance because hydrolysis of a reactive dye in aqueous system is almost inevitable. If the presence of water in the dye bath is reduced or eliminated, the dye hydrolysis could be minimised or avoided leading to higher dye fixation on cotton. Higher dye exhaustion and better fixation were achieved when aqueous-alkaline - pre-swollen cotton was dyed in DMF-TCE solvent mixture [14,15]. Acetone and the mixtures of acetone-TCE assisted by a small proportion of water or DMF was also suggested for the application of reactive dyes on water or aqueous-alkali-swollen cotton [17]. The work on the application of acid and direct dyes on water swollen-solvent exchanged (WSSE) cotton from DMF-TCE solvent mixtures revealed that with the increase in TCE content in the solvent dye bath, the dye-uptake on the fibre was increased. This increase in dye uptake was attributed to the decrease in dye solubility in the solvent mixture. The present work is an extension of the earlier study on the application of anionic dyes on cotton from DMF-TCE mixtures. For this purpose three anionic dyes (CI Acid Red 88, CI Acid Red 13 and CI Acid Red 18) having the same structure but number of sulphonic acid groups varying from 1 to 3 were specifically selected. It was postulated that the transfer of the dye from external phase to the internal liquid phase closely associated with the fibre (which was essentially DMF) takes place due to solubility difference, followed by Langmuir adsorption. The above hypothesis was based on the experimental observations on the electrokinetic character of cotton in the solvent medium, analysis of the adsorption isotherms and the dyeing behaviour of oxidized cotton. An attempt was also made to explain the dyeing observations on the basis of solubility parameter concent. To understand the state of dye in solution the aggregation behaviour of the dyes in DMF-TCE solvent mixtures was also studied.

The thesis has been divided into seven chapters. First chapter relates to the general introduction and a review of literature.

In the second chapter the zeta potential existing at the interface of WSSE cotton and DMF,TCE and their mixtures was determined using streaming potential technique, and its effect on dyeing was discussed.

In chapter three, to understand the dyeing mechanism, the equilibrium dyeings were carried out at 40°C from DMF-TCE mixtures. The adsorption isotherms were constructed and interpreted in terms of distribution of dye between the dye bath and the solvent closely associated with the fibre followed by Langmuir adsorption on cotton. Using Langmuir equation affinity values were calculated. It was observed that the dye affinity increased with the increase in sulphonic acid groups in dye molecule and also with the increase of TCE content in the solvent mixture.

The study of equilibrium adsorption of the dyes on oxidized cotton from DMF-TCE mixtures as reported in chapter four revealed that at any DMF-TCE ratio the dye uptake expressed in terms of percent exhaustion was decreased with increase in carboxyl content. However, with the increase in TCE content in the solvent mixture the dye uptake was increased. Although there was increase in dye uptake with the increase in TCE content in the solvent mixture, for any particular dye, the repulsive effect of carboxyl groups, as determined from the extent of reduction in dye uptake was found to be almost same. This fact revealed that the internal liquid closely associated with the fibre was essentially DMF, from which dyeing takes place. The reduction in dye uptake due to repulsive effect of carboxyl groups varied with the number of sulphonic acid groups in the dye molecule. It was noticed that the presence of carboxyl groups changed the isotherm from Langmuir to Sigmoid shape.

In chapter five some of the basic principles of solubility parameter concept and its effect on dyeing behaviour have been discussed. The solubility parameters of the dyes were theoretically calculated by Van Krevelen's method. The solubility parameters of cotton, DMF and TCE were taken from literature. The solubility parameter of solvent mixtures were calculated using standard equation. The solubilities of dyes in DMF and DMF-TCE mixtures and dyeing behaviour of cotton from DMF-TCE mixtures were related to solubility parameter values. However, in order to explain all the dyeing observations it was thought to be essential to divide the total solubility parameter of cellulose,dyes and solvent mixtures into solubility parameter due to association forces (δ_A) and solubility parameter due to dispersion forces (δ_d). The δ_d-values were calculated from refractive indices. The refractive indices of the dyes were theoretically determined with the help of model compounds using Lorentz and Lorenz equation. For solvent mixtures the refractive indices were experimentally determined and the refractive index of cotton was taken from literature. δ_A-values were calculated using a standard equation. The total picture on the dyeing behaviour of cotton from solvent mixtures emerged from the above concept revealed that the dye adsorption was mainly governed by dispersion forces. This fact was experimentally verified by studying the effect of temperature on dye uptake. It was observed that the temperature had no effect on dye uptake which suggested that the adsorption process was mainly governed by the weak attractive forces like dispersion forces.

The sixth chapter deals with the aggregation behaviour of the dyes in DMF-TCE solvent mixtures. For this purpose, a new technique, namely, quasi-elastic light scattering (QLS) was employed. It was observed that the aggregation tendency of the dyes in DMF-TCE mixtures was dependent on the TCE content and on the number of sulphonic acid groups and their position in the dye molecule.

The salient features of the dyeing systems are summarised in the concluding chapter.

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CHAPTER 5 SOLUBILITY PARAMETER

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