Some New Metal Complex Solvents for Use as Analytical Agents for Wool and Silk

W. B. ACHWAL, H. J. GORE, P. C. JAIN & V. P. MOHITE
Department of Chemical Technology, University of Bombay, Bombay 400 019

Received 16 January 1976; accepted 31 January 1976

Cadoxen and zincoxen solvents have been found to dissolve wool and silk fibres. The dye content of the dyed material can be estimated by colorimetry of the solutions. With most dyeings, except yellow and orange, the cadoxen method is preferable. The extent of canary yellow coloration can be estimated using zincoxen. Wool solutions have extremely low specific viscosity and wool cannot be reprecipitated. Paper chromatography as well as TLC indicate the absence of amino acids. Light scattering measurements, however, show that wool molecules dissolved in zincoxen retain their polymeric nature.

O n account of its colourless nature and high stability of its cellulose solutions, the solvent cadoxen (tris-ethylenediamine cadmium dihydroxide) has found many analytical applications. Methods have been standardized for the determination of the degree of polymerization (DP), estimation of dyes as well as optical brighteners, quantitative analysis of fibre blends as well as to get information about dye-fibre bond. Wool and silk fibres were found to dissolve in cadoxen and zincoxen and estimation of the dye content of dyed fibres has been attempted by the measurement of absorbance of solutions. The possibility of estimating canary yellow coloration using zincoxen solvent has been investigated. The polymeric state of wool after dissolution in cadoxen or zincoxen has been studied through the measurement of viscosity, light scattering, paper and thin layer chromatography and other techniques.

Experimental Procedure

Cadoxen solvent — Solvent containing 4.7% cadmium was prepared by the gradual addition of cadmium oxide to cooled 28% aqueous ethylenediamine.

Zincoxen solvent — Solvent containing 1.9% zinc and 28% ethylenediamine was prepared in a similar manner.

Dyeing — Purified wool yarn was cut into 1 cm length and dyed with different dyes at liquor-goods ratio of 100:1 under optimum conditions as recommended by the manufacturers. Colorimetric measurements on wool solutions were carried out using a Hilger Biochem absorptiometer.

Chromatography — Ascending paper chromatography was done using Whatman paper No. 1 and TLC on glass plates covered with silica gel G.

Viscosity — The flow time of solutions was measured in Ubbelhode type viscometer in a water thermostat at 30 ± 0.1°C.

Light scattering — Measurements were carried out using a Brice Phoenix photometer at 30°C at wavelength 4360Å at 90°. The refractive index was measured using Brice Phoenix refractometer at 30°C at the same wavelength.

Fibre materials — The wool samples studied included yarn made from Australian merino wool and 5 types of Indian wools, viz. R. C. (Rembullet-Chokla cross-breed), Nali, Chokla, Malpura and canary stained Nali. The above wool samples as well as two types of silk yarn were purified and conditioned before use.

Results

Dissolution of fibres — The solvent power of cadoxen and zincoxen for wool and silk is limited and quantitative dissolution was possible only to the extent of about 0.2 g/dl. Australian merino wool dissolved in about 4 hr, while Indian wools, particularly the canary stained one, required 18-24 hr. The time for dissolution in zincoxen is much longer (72-96 hr). Wool solutions in cadoxen are pale yellowish and tend to form yellow precipitate on storage, but solutions in zincoxen are colourless and show no precipitation even on prolonged storage.

Estimation of dye content — Initially, the stabilities of dyes of different classes were studied. Direct, metal-complex, most of the acid dyes and reactive dyes were stable, but all basic dyes and some blue as well as green acid dyes were unstable. The instability in both solvents was due to alkaline nature of the ethylenediamine present in them. The dye content of wool dyed in different depths with typical dyes from each class was estimated by dissolving 10-20 mg of material in 20 ml solvent for 24 hr and measuring the absorbance of the solution. Colorimetric measurements of the solutions in cadoxen were done using undyed wool solution as blank to compensate for yellow coloration. The dye content was calculated by reference to the corresponding calibration curves.

With orange and yellow dyeings, the values obtained by the cadoxen method were inconsistent.
and more accurate results were obtained by the zincoxen method. Both cadoxen and zincoxen methods gave 5-10\% higher value of dye content for acid and direct colour dyings as compared to the values obtained by pyridine extraction.

Estimation of canary yellow coloration — As merino and other types of white wools gave a colourless solution in zincoxen, an attempt was made to estimate the canary yellow coloration by colorimetric measurement of solutions (0.2 g/dl) in zincoxen. Three samples of canary stained Nali wools having different depths of yellow coloration were selected and the absorbances measured.

The values of absorbance increase progressively with visual assessment.

Reactive dyings on wool — The dissolution in cadoxen of wool dyed with Procion Yellow HA, Procion Brilliant Purple H3RS, Procion Orange MG and Procion Brilliant Red M5BS at 2 and 10\% shades was compared with that of undyed wool as well as wool finished with dimethyl cyclo ethylene urea (DMEU). For all samples, 50 mg material was shaken with 25 ml cadoxen and the portion undissolved after 6 hr was estimated gravimetrically.

No significant difference in the extent of dissolution was observed for all dyed wools as well as undyed wools. In contrast to this, DMEU finished samples showed considerably lower dissolution. The alkali solubility as well as urea-bisulphite solubility values for resin treated samples were appreciably lower than for undyed wool, while all dyed samples had somewhat higher values. TLC of dyed wool solutions in methyl glycol-acetone-water showed only spots for hydrolysed dye and no dye-coloured spot at start as in the case of dyed cotton samples.

Study of solution properties — Viscosity measurements were carried out on solutions of different types of wool in cadoxen and zincoxen in Ubbelhode viscometers. The relative viscosity values for different types of wools at 0.2 g/dl concentration were very low (1.03-1.04). Measured values of flow time at different concentrations in the range 0.05-0.2 g/dl were very close and indicated intrinsic viscosity in the range 0.1-0.2. This extremely low value as compared to 12 for cotton in cadoxen suggested the possibility of breakdown of the polypeptide chain during dissolution, which was studied chromatographically.

Paper chromatography was done using two eluant systems: (1) Phenol-water, and (2) butanol-acetic acid-water and TLC using phenol-water system. The results for solutions of different types of wools in both cadoxen and zincoxen were identical and failed to show any characteristic spots for amino acids. The solvent itself caused some interference by giving long spots in certain regions due to the reaction of ethylenediamine and metal complex with the ninhydrin staining agent. On dialysing solutions of wool, this interference was eliminated and wool hydrolysate as well as individual amino acids did give characteristic spots in the presence of the solvent, except in the above interference region. Even on prolonged storage for many months, wool solutions in cadoxen and zincoxen showed no traces of the formation of amino acids as decomposition products.

Light scattering measurements were then carried out on wool solutions in zincoxen only, as solutions in cadoxen are yellow coloured and turbid. The value for refractive index of zincoxen was 1.387 and the refractive index increment $dn/dc = 0.0387$ ml/g. The latter measurement is inaccurate due to low concentration of the polymer. The value of optical constant is thus $H = 4.38 \times 10^{-4}$.

From the plot of $C_f/\theta$ against $C$, the value of the intercept was found to be about 1.8, giving a weight average molecular weight of more than 10$^4$. From the value of the slope, the value of the second virial coefficient was calculated to be about $0.9 \times 10^{-4}$. The small magnitude of $\Lambda_2$ is consistent with low solubility of the sample in zincoxen.

Information about conformation of the molecule was obtained by the dissymmetry method assuming random coil configuration of the polymer chains in solution. From the limiting value of $Z$ at $C \rightarrow 0$, the value of the root mean square end to end distance was found to be about 1100 Å and the radius of gyration about 450 Å.

**Discussion**

Solvent power for wool — The metal concentration in stable zincoxen solvent is only 1.9\% as compared to 5\% cadmium in cadoxen, which explains the lower solvent power of zincoxen for both natural cellulose as well as protein fibres. The formation of yellow coloured solution and gradual yellow precipitation are due to cadmium sulphide formed as a result of disruption of -S-S- links. Silk, on the other hand, contains very small amounts of cystine and gives a colourless solution, as zinc sulphide is white and has a higher solubility.

Estimation of dye content — The estimation of direct and acid dyes on wool is usually carried out with 25\% aqueous pyridine at boil. The higher values

<table>
<thead>
<tr>
<th>Sample colour</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pale yellow</td>
<td>0.06</td>
</tr>
<tr>
<td>Medium yellow</td>
<td>0.09</td>
</tr>
<tr>
<td>Dark yellow</td>
<td>0.13</td>
</tr>
</tbody>
</table>

**Estimation of dye content**

**Discussion**

**Table 1 — Absorbance Values in Zincoxen for Canary Stained Wools**

<table>
<thead>
<tr>
<th>Sample colour</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pale yellow</td>
<td>0.06</td>
</tr>
<tr>
<td>Medium yellow</td>
<td>0.09</td>
</tr>
<tr>
<td>Dark yellow</td>
<td>0.13</td>
</tr>
</tbody>
</table>

**Table 2 — Dissolution of Reactive Dyed Wool in Cadoxen**

<table>
<thead>
<tr>
<th>Wool sample</th>
<th>Dissolution</th>
<th>Urea bisulphite solubility %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undyed</td>
<td>100</td>
<td>18</td>
</tr>
<tr>
<td>All dyed samples</td>
<td>&gt;90</td>
<td>20-30</td>
</tr>
<tr>
<td>DMEU treated (20 g/litre)</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>DMEU treated (200 g/litre)</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 3 — Light Scattering of Wool Solutions**

<table>
<thead>
<tr>
<th>$C \times 10^4$ g/ml</th>
<th>$C_f/\theta$</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.5</td>
<td>0.72</td>
<td>2.80</td>
</tr>
<tr>
<td>11.6</td>
<td>0.62</td>
<td>2.55</td>
</tr>
<tr>
<td>7.75</td>
<td>0.46</td>
<td>2.42</td>
</tr>
<tr>
<td>3.87</td>
<td>0.26</td>
<td>1.98</td>
</tr>
</tbody>
</table>
obtained by colorimetric estimations in cadoxen as well as zincoxen are due to complete dissolution of fibre, making dye available in sufficient quantity for estimation as compared to incomplete extraction in pyridine. Metal complex dyes are estimated by initial zincoxen of the dyings with oxalic acid followed by pyridine extraction, but without much success.

For these dyeings, estimation of absorbance of solution of the dyed material in these solvents would be more reliable. Reactive dyeings can also be estimated accurately by this method and no other suitable method has been reported in literature. With most dyeings, except yellow and orange shades, estimation by colorimetry in cadoxen using solution of undyed wool as blank will be more convenient and quicker. Dyeings in all shades on silk can be estimated in cadoxen.

Estimation of canary yellow coloration — The problem of canary yellow coloration is encountered in many parts of the world. In India, most of the sheep in Rajasthan, U.P., Punjab and North Gujarat produce canary stained varieties. Quantitative assessment of the yellow coloration is desirable for grading as well as selection of dyes to get matching. Measurement of absorbance of solutions of typical canary yellow dyeings in cadoxen was found to be practicable and reliable, giving values consistent with visual assessment. For exact quantitative estimation, calibration with isolated pigment solutions will be necessary. Isolation of the pigment after treatment of wool with conc. hydrochloric acid or ammonium hydroxide gives a modified form of pigment. It may be possible to isolate the pigment from solutions in zincoxen.

Dissolution of reactive dyed wool — A study of the kinetics of dissolution as well as chromatography of solutions of reactive dyed cotton gave information about the possibility of crosslinking as well as stability of the dye-fibre bond\(^6\). The presence of crosslinks in dyed or finished cotton was found to restrict considerably the swelling and dissolution in cadoxen. With wool dyed with difunctional reactive dyes, however, no restraint on dissolution is observed, suggesting the absence of crosslinks due to milder conditions used in dyeing and steric considerations. The disruption of the dye-fibre bond during dissolution, as shown by chromatography, indicates higher sensitivity of the -NH-D linkage as compared to the -O-D linkage in celluloses.

Behaviour of wool solutions — Viscosity measurements were restricted to the very low concentration range due to limited solubility in both solvents and gave very low values (0.1-0.2) for intrinsic viscosity. Very little information on the viscosity of wool solutions is available in literature and the values mentioned are of a similar order\(^9\).

Light scattering data conclusively proved the polymeric nature of wool dissolved in zincoxen, as shown by high molecular weight in the range of \(10^6\) and large values of root mean square end to end distance and radius of gyration. No such data can be measured in cadoxen, as wool solutions have limited stability and yellow colour and form a precipitate, but the behaviour can be expected to be similar.

Chromatography of wool solutions in both the solvents even on long storage showed that no traces of amino acids are formed. However, wool solutions cannot be precipitated by the addition of acids as well as aliphatic alcohols, as is possible with cellulose solutions. Thus, although cadoxen and zincoxen are able to dissolve cellulose as well as natural protein fibres, the physico-chemical behaviour of dissolved molecules is radically different.

Acknowledgement

One of the authors (W.B.A.) is thankful to the Bombay University and the Department of Chemical Technology for deputing him to participate in the Fifth International Wool Textile Research Conference and to DAAD for financial support. The authors’ thanks are also due to Dr C. K. Patel of the Chemistry Department, Sardar Patel University, Gujarat, for carrying out the light scattering measurements in a short time.

References