Dyeability of C. I. Disperse Violet 1 on Polyester Fiber in Alkanes as Dyeing Media

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Abstract: In order to survey the possibility of an organic solvent as a dyeing medium, the dye uptake of C. I. Disperse Violet 1 on polyester fiber in 31 kinds of solvents including water was investigated. The dye uptake in alkanes was observed to be much higher than that in other organic solvents. As the number of carbon atoms in alkanes decreased, the dye uptake increased drastically. It was shown that dye uptake was linearly and inversely proportional to the solubility of the dye in various organic solvents in a logarithmic plot. It is very interesting that unless their flammable properties some alkanes are considered to be the excellent dyeing media for a non-aqueous dyeing system. Besides the practical aspects, the results obtained in this study may be beneficial in assisting the further development of non-aqueous dyeing systems.

1. Introduction

Since the oil and energy crisis of 1973, there has been an increasing interest in the use of organic solvents to replace water as the dyeing medium. Tetrachloroethylene has been regarded as the most suitable solvent for this purpose. Accordingly, the development of non-aqueous solvent dyeing technology for polyester fiber using tetrachloroethylene has received much attention and numerous papers and articles have been published on this topic [1-5]. Unfortunately, very little of this activity has been transferred to commercial coloration applications. The main reason for this was that disperse dyes dissolved fairly readily in tetrachloroethylene and thus had to be applied in the state of solution rather than dispersion. This high dye solubility, therefore, hindered further development.

In recent years interest in this area has been rekindled as a result of increasing social pressure to minimize pollution in the environment and the rising cost of water. In 1991, a new solvent-dyeing system was launched based on the use of supercritical carbon dioxide as a dyeing medium for disperse dyes. Currently, there are a few publications on this topic including the development of commercial machinery. However, progress is still in its infancy because of the high pressure to achieve successful disperse dyeing using 30 MPa [6,7].

In this study a wide variety of organic solvents were surveyed as possible dyeing medium for polyester fiber, and alkanes were focused because it was discovered that the dye uptake of C. I. Disperse Violet 1 on polyester fiber in alkanes was comparable to that in water. The dye uptakes on polyester fiber were discussed in relation to the solubilities of dye in organic solvents.

2. Experimental

2.1 Materials

The substrate used in this experiment was a plain-weaved polyester fabric (75 denier/36 filaments, 176 × 82 yarns/inch) which was scoured in a 0.1% nonionic surfactant solution at 90°C for 60 min and then rinsed with distilled water repeatedly. The dye,
C. I. Disperse Violet 1 (1,4-diaminoanthraquinone), was extracted with acetone in a Soxhlet extractor and recrystallized from ethanol. The organic solvents were the first grade and were used without further purification.

2.2 Methods

2.2.1 Dyeing

Polyester fabrics (0.2 g) were dyed in tightly sealed stainless steel pots housed in an Auto Textile Dyeing Machine (Korea Science Industry Co.,) which contained 0.005 g of the dye and 50 mL of the solvent in the absence of any auxiliaries. The initial temperature for the dyeing process was 30°C, then over a period of 40 min this was raised to 130°C and finally the temperature was maintained at 130°C for 60 min. After dyeing the dyed samples were completely washed with acetone and dried in a vacuum.

The dried samples were weighed carefully and then extracted with N,N-dimethylformamide at 95°C until they became colorless. The dye concentration in the extract was measured spectrophotometrically (UV-2100 spectrophotometer, SHIMADZU Co., Japan).

2.2.2 Solubility of Dye

An excess amount of the dye was dissolved in 10 mL of each solvent at 15°C for over 48 hours. Thereafter, the solutions were centrifuged at the same temperature to precipitate any undissolved dye and 1 mL of the supernatant solution was taken and diluted with a liberal amount of the solvent. The concentration of the dye was then measured spectrophotometrically, and finally the solubility of the dye in each solvent was calculated.

3. Results and Discussion

To investigate the feasibility of a solvent as a dyeing medium, 31 different kinds of solvents including water were tested as media for dyeing polyester fiber with C. I. Disperse Violet 1. The results are shown in Fig. 1. The dye uptakes in most organic solvents were very low (0 ~ 3 mmole/kg fiber). However, that in hexane (13.18 mmole/kg fiber) was comparable to that in water (16.09 mmole/kg fiber) and superior to that in tetrachloroethylene (1.56 mmole/kg fiber). It is interesting to note that hexane is a good dyeing medium for polyester. Although tetrachloroethylene has been generally recognized as the most effective solvent for dyeing polyester fiber and the extensive research with tetrachloroethylene has been focused over the last few decades, tetrachloroethylene exhibited poor dye uptake.

Consequently, several homologous series of alkanes around hexane were then investigated, as shown in Fig. 2. In the range from pentane to decane

Fig. 1 Dye uptake of C. I. Disperse Violet 1 on polyester fiber in various organic solvents at 130°C for 1 hour.

Fig. 2 Relationship between the number of carbon atoms of alkanes and the dye uptake of C. I. Disperse Violet 1 on polyester fiber at 130°C for 1 hour.
used as a dyeing medium, as the number of carbon atoms in the alkane decreased, the dye uptake gradually increased and finally the dye uptake in pentane exceeded that in water.

Isoalkanes and cycloalkane exhibited different dye uptakes. That is, isoalkanes showed a higher value, whereas cycloalkane gave a lower value compared with normal alkanes.

It is well known that in a water-based system dyeing is actualized as hydrophobic disperse dyes are dissolved in the hydrophobic polyester more easily than in water which is a hydrophilic solvent. Therefore, the solubility of a dye in a solvent is a very important factor for determining dye uptake in a fiber-solvent system. In this study the dye solubility in each of the solvents tested as a dyeing medium was also measured in relation to dye uptake. The results are illustrated in Figs 3 and 4.

**Fig. 3** Relationship between the dye uptake on polyester fiber at 130°C and the solubility of C. I. Disperse Violet 1 in various organic solvents at 15°C.

In Fig. 3 the dye uptake in fiber is inversely proportional to the solubility of the dye in the dyeing medium. The dye uptake in water is very high because only extremely small amount of dye is dissolved, whereas dimethylsulfoxide indicates a high solubility and the dye uptake is nil. It was observed that while solubility gradually increased, dye uptake dramatically decreased.

Figure 4 shows the dye solubility in relation to the number of carbon atom in alkanes. As the number of carbon atom in alkanes increased, the solubility of dye in alkane increased, and the dye uptake decreased as shown in Fig. 2. The solubility of a dye in a solvent sensitively affects dye uptake, such that dye uptake would seem to be in exponentially inverse proportion to solubility. To observe this relation more clearly, a logarithmic scale is plotted in Fig. 5 which illustrates a linearly inverse proportion. This

**Fig. 4** Relationship between the number of carbon atoms of alkanes and the solubility of C. I. Disperse Violet 1 in alkanes at 15°C.

**Fig. 5** Logarithmic plot of the solubility of C. I. Disperse Violet 1 in various organic solvents at 15°C and the dye uptake at 130°C.
also confirms that the dye uptakes in alkanes are higher than those in the other solvents. Water is the only solvent that deviated from the straight line, possibly because water, an inorganic solvent, has different properties from the other organic solvents.

The difference of dye solubility in each alkane could be explained by the density of alkane. Tables 1 [8] and 2 present densities of alkanes and solubilities of the dye in alkanes. Alkanes consist of the same kinds of atoms, however, their densities are different according to the number of carbon atoms, that is, the larger the alkane, the higher the density.

Table 1 Density of alkanes [8].

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Density (g/mL, 20°C)</th>
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<tbody>
<tr>
<td>n-Pentane</td>
<td>0.626</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>0.619</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.655</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.779</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.684</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.699</td>
</tr>
<tr>
<td>iso-Octane</td>
<td>0.688</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>0.718</td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.730</td>
</tr>
</tbody>
</table>

a) 2-Methylbutane
b) 2,2,4-Trimethylpentane

As the density of an alkane increases, the number of constituent atoms in a unit volume increases, and the molecule becomes more compact. This then strengthens the interaction between an alkane and a dye molecule, and as a result the solubility of a dye increases. In the case of isoalkanes and cycloalkane densities also vary due to branching or cyclization. As a result of branching and cyclization, the densities of isoalkanes are lower and that of cycloalkane is higher compared to those of normal alkanes. This tendency corresponds well with the dye solubilities in alkanes as shown in Table 2.

Generally, polyester fiber is dyed at a relatively higher temperature than other fibers due to its hydrophobicity and structural compactness. Therefore, many studies have reported on methods that can increase dye uptake by using organic solvents as carriers that plasticize the polyester fiber, or by loosening the internal structure of the fiber by pretreatment with organic solvents [9-13]. With solvent dyeing that uses organic solvents as dyeing media, the solvents can plasticize the polyester fiber to different degrees, which could result in different dye uptakes for each solvent.

Ribnick and his co-workers measured the glass transition temperature (T_g) of polyester in various organic solvents using the dynamic shrinkage method [14]. The polyester fiber was immersed in an organic solvent, then the fiber was shrunk. The shrinkage of the fiber was measured under a constant rate of heating. The measured shrinkage was plotted against the temperature of the solvent. The linear portion of the shrinkage curve was extrapolated to a zero-shrinkage temperature (T_0). According to this experiment, the zero-shrinkage temperature is identified with the T_g of a fiber in the solvent.

The data for eight solvents that were used in both this study and Ribnick's is shown in Table 3. The T_g of polyester versus the dye uptake of C. I. Disperse Violet 1 on polyester fiber at 130°C in each solvent is plotted in Fig. 6. However, there is no evidence of any relation. This indicates that at a high temperature of 130°C the structure of polyester is already considerably relaxed and the decrease in the T_g of polyester due to solvents seems to be very small relative to the effect of solubility, and thus can be considered negligible.
Table 3  Estimation of $T_s$ of polyester in various organic solvents by means of dynamic shrinkage [14].

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$T_s$(°C)</th>
<th>$\Delta T_s$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry (in air)</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>30</td>
<td>53</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>20</td>
<td>63</td>
</tr>
<tr>
<td>Toluene</td>
<td>20</td>
<td>63</td>
</tr>
<tr>
<td>Dimethylsulfoxide</td>
<td>-15</td>
<td>98</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>-33</td>
<td>116</td>
</tr>
<tr>
<td>Pyridine</td>
<td>-67</td>
<td>150</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>-72</td>
<td>155</td>
</tr>
<tr>
<td>Chloroform</td>
<td>-143</td>
<td>226</td>
</tr>
</tbody>
</table>

Fig. 6 Relationship between the $T_s$ of polyester fiber in solvents [14] and the dye uptake of C. I. Disperse Violet 1 at 130°C.

4. Conclusion

The dye uptake of C. I. Disperse Violet 1 on polyester fiber in 31 kinds of solvents including water was investigated. The dye uptake in alkanes was much higher than that in the other organic solvents. As the number of carbon atom in alkanes decreases, dye uptake increases drastically. From the dye solubility data in various organic solvents, it was clearly shown that dye uptake is linearly and inversely proportional to solubility in a logarithmic plot. The solubility of the dye in an alkane could be explained in relation to the density of the alkane. Accordingly, as the density of an alkane increases, the dye solubility increases and the dye uptake decreases.

Alkanes such as heptane and hexane are the most suitable solvents practically for the non-aqueous dyeing of polyester fiber except for their flammable properties. More focus should be given to the practical applications of these results considering many chemical and food technologies that use hexane as an extracting solvent and the recent enthusiasm for supercritical carbon dioxide dyeing which requires very high pressure.

References