

The Effect of Carriers on the Dyeing of Courtelle S

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ABSTRACT

The extent to which uptake of CI Basic Blue 3 on to Courtelle S was enhanced by seven carriers based on benzyl alcohol was proportional to the amount of each carrier adsorbed by the fibre. Maximum dye uptake coincided with the maximum uptake of each carrier by the fibre. The maximum that occurred in the extent of carrier uptake by the substrate has been interpreted in terms of the aqueous solubility of the carrier and the solubility parameter concept.

1 INTRODUCTION

Several workers have demonstrated that during carrier dyeing, the uptake of cationic dyes^{1,2} and disperse dyes^{3,4} on acrylic fibres, as well as the uptake of disperse dyes on to polyester⁵⁻⁸ and triacetate⁶ fibres, reached a maximum value that corresponded to a particular concentration of carrier applied. Balmforth *et al.*⁷ concluded that at carrier concentrations in excess of that which gave maximum disperse dye uptake onto polyester, undissolved carrier was present in the dyebath as a third phase in which the dye remained undissolved, thereby reducing dye uptake. Balmforth's suggestion was endorsed by Ingamells and Narasiham⁸ from studies of the effect of benzyl alcohol on the dyeing of polyester with *p*-aminoazobenzene, although these workers also proposed that maximum dye uptake may well represent a change in the molecular structure of the fibre. In studies of the effects of *o*-phenylpheonol² and benzyl alcohol¹ on the uptake of several basic dyes onto Courtelle S at 98°C, it was found that for both carriers, dye uptake

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reached a maximum value that corresponded to the aqueous solubility of the carrier at 98°C. Previous studies by the present authors on the effects of benzyl alcohol on the uptake of two cationic dyes on Courtelle S tow^{9,10} and of three derivatives of benzyl alcohol on the adsorption of CI Basic Blue 3 on Courtelle S tow¹¹ demonstrated that the extent to which dye uptake was enhanced by the four carriers was proportional to the amount of each carrier adsorbed by the fibre, with maximum dye uptake coinciding with maximum uptake of carrier by the fibre. Although the maximum extent of uptake of each carrier corresponded approximately to the aqueous solubility of the carrier at the dyeing temperature (80°C) used,⁹⁻¹¹ the solubility parameter concept was employed¹¹ to demonstrate that the maximum extent of carrier uptake was related to the δ_a value of the carrier and, therefore, that polar forces primarily contribute to carrier–acrylic fibre interaction.

The purpose of the present work was to extend these earlier studies⁹⁻¹¹ by investigating the effects of three other derivatives of benzyl alcohol on the uptake of CI Basic Blue 3 on Courtelle S tow.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Fibre

A commercial sample of Courtelle S tow supplied by Courtaulds Fibres was used; the fibre was scoured prior to use as previously described.¹⁰

2.1.2 Carriers

Each of the three carriers used, namely 4-methoxybenzyl alcohol, 4-isopropylbenzyl alcohol and 4-biphenylmethanol, was of laboratory grade purity obtained from Sigma-Aldrich.

2.1.3 Dye

A sample of pure Maxilon Blue 5G (I) (Ciba-Geigy) (CI Basic Blue 3) was kindly supplied by Courtaulds Fibres Plc. The purity of the dye was checked using the method described earlier.¹⁰

All other reagents were of 'Analar' grade purity.

2.2 Procedures

2.2.1 Treatment of acrylic tow with carrier

Each of the three carriers was applied to Courtelle S tow following the procedure previously described 10,11 using a 300 cm³ capacity stainless steel

dyepot housed in a Zeltex Polycolor PC1000 laboratory dyeing machine (Zeltex, Switzerland). The concentration ranges used for the carriers were 5, 10, 20, 30, 40, 50, 60 and 70 cm³ dm⁻³ for 4-methoxybenzyl alcohol, 0.5, 1, 2, 3, 4, 5, 10 and 15 cm³ dm⁻³ for 4-isopropylbenzyl alcohol and 0.5, 1, 2, 3, 4, 5, 10 and 15 g dm⁻³ for 4-biphenylmethanol.

2.2.2 Determination of carrier uptake on to Courtelle S tow

The extent of uptake of each of the three carriers was determined using the procedure described previously 10,11 employing a Varian 3300 Gas Chromatograph (Varian, USA) interfaced to an NEC 386 SX personal computer (NEC, Japan) and equipped with a DB wax Megabore column (film thickness 1 μ m, length 30 m). The temperatures for optimum separation of the three carriers were found to be 200°C for 4-methoxybenzyl alcohol, 190°C for 4-isopropylbenzyl alcohol and 230°C for 4-biphenylmethanol, which resulted in retention times of 1.61, 3.30 and 2.84 min respectively.

2.2.3 The effect of carriers on dye uptake

The procedure previously described 10,11 was employed to determine the effect of each of the three carriers on the uptake of CI Basic Blue 3 using 300 cm³ capacity stainless steel dyepots housed in a Zeltex Polycolor PC1000 laboratory dyeing machine. Each dyebath comprised a 20 cm³ aliquot of a stock aqueous (distilled water) solution of CI Basic Blue 3 $(7 \times 10^{-3} \text{ mol dm}^{-3})$ and an appropriate amount of carrier (5, 10, 20, 30, 40, 50, 60 or 70 cm³ dm⁻³ for 4-methoxybenzyl alcohol, 0.5, 1, 2, 3, 4, 5, 10 or 15 cm³ dm⁻³ for 4-isopropylbenzyl alcohol and 0.5, 1, 2, 3, 4, 5, 10 or 15 g dm⁻³ for 4-biphenylmethanol). After first rinsing in water and then in acetone to remove surplus dye and carrier following the procedure described earlier, 10,11 the dyed material was dissolved in DMF and the ensuing solution acidified with glacial acetic acid; the absorbance of the solution was measured at 649 nm (the λ_{max} of the dye in this medium) using a Pye-Unicam PU 8600 UV/visible spectrophotometer as previously described. 10,11 The concentration of dve in the fibre (D_e) was obtained by reference to the appropriate extinction coefficient of the dye $(8.95 \times 10^6 \,\mathrm{dm^3 \,mol^{-1} \,m^{-1}})$ in acidified DMF (20% v/v acetic acid/DMF) solution.

2.2.4 Determination of the aqueous solubility of each carrier at $80^{\circ}C$ This was carried out following the procedure described earlier 10,11 using sealed $300\,\mathrm{cm^3}$ capacity stainless steel dyepots housed in a Zeltex Polycolor PC1000 laboratory-scale dyeing machine. In the case of 4-biphenylmethanol, dilution of the $10\,\mathrm{cm^{-3}}$ aliquot of the heated dispersion was effected with $90\,\mathrm{cm^3}$ of a 50% v/v methanol/stock aqueous buffer solution. The absorbance of the carrier solutions was measured at the respective λ_{max} of

each carrier (272 nm for 4-methoxybenzyl alcohol, 261 nm for 4-isopropylbenzyl alcohol and 254 nm for 4-biphenylmethanol) using a Pye-Unicam PU 8600 UV/visible spectrophotometer. The solubility of the carrier was then determined by reference to the appropriate extinction coefficient of the carrier previously measured in the appropriate solvent.

3 RESULTS AND DISCUSSION

Figures 1–3 show the uptake of CI Basic Blue 3 onto Courtelle S, as well as the uptake of carrier onto the substrate as a function of the concentration of each of the three carriers applied. It is evident that each of the three carriers used enhanced the uptake of CI Basic Blue 3 onto Courtelle S tow at 80°C, and also the extent of the enhanced dye uptake imparted by each carrier corresponded to the extent of uptake of each carrier onto the substrate. Figures 1–3 clearly show that the plot of dye uptake as a function of the concentration of 4-methoxybenzyl alcohol, 4-isopropylbenzyl alcohol and 4-biphenylmethanol, respectively, are superimposable onto those of the plots of uptake of each carrier as a function of the concentration of carrier. These findings therefore demonstrate that the extent of carrier action imparted to CI Basic Blue 3 by each of the three derivatives of benzyl alcohol under consideration is clearly related to the concentration of each carrier

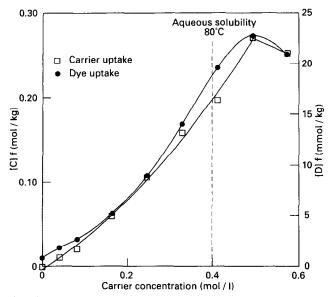


Fig. 1. Uptake of CI Basic Blue 3 and also 4-methoxybenzyl alcohol onto Courtelle S as a function of the concentration of 4-methoxybenzyl alcohol applied.

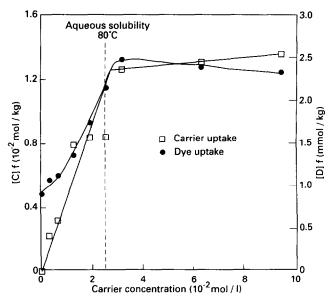


Fig. 2. Uptake of CI Basic Blue 3 and also 4-isopropylbenzyl alcohol onto Courtelle S as a function of the concentration of 4-isopropylbenzyl alcohol applied.

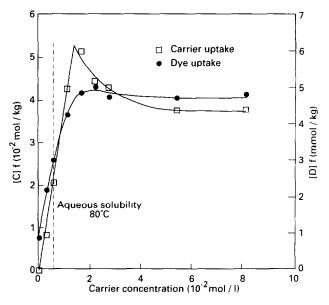


Fig. 3. Uptake of CI Basic Blue 3 and also 4-biphenylmethanol onto Courtelle S as a function of the concentration of 4-biphenylmethanol applied.

present in the fibre; further support for this finding is provided by the linear relationship obtained between the extent of enhanced dye uptake and the concentration of 4-methoxybenzyl alcohol, 4-isopropylbenzyl alcohol and also 4-biphenylmethanol adsorbed by the fibre (Fig. 4). The findings displayed in Figs 1–3 concur with those of previous studies of the effects of benzyl alcohol¹⁰ and of 3-phenyl-1-propanol, 4-methylbenzyl alcohol and phenethyl alcohol¹¹ on the dyeing of Courtelle S with cationic dyes.

Figures 1–3 also show that the uptake of each of the three carriers under consideration onto Courtelle S tow at 80°C increased with increasing concentration of carrier applied upto a maximum value, after which uptake decreased with further increase in concentration of carrier. As previously suggested, 1.2.9–11 Figs 1–3 imply that maximum carrier uptake may be related to the aqueous solubility of the carrier, in that the maximum extent of uptake of each of the three carriers coincided approximately with the aqueous solubility of each compound at 80°C (indicated by the vertical dashed line in Figs 1–3), the temperature at which treatment had been carried out. However, it is evident from Figs 1–3 that for each of the three carriers employed, maximum carrier uptake occurred at a concentration in excess of the measured aqueous solubility of the carrier.

Since the purpose of this investigation was to further extend the previous studies carried out using benzyl alcohol^{9,10} and also 3-phenyl-1-propanol, 4-methylbenzyl alcohol and phenethyl alcohol, ¹¹ the results obtained for 4-

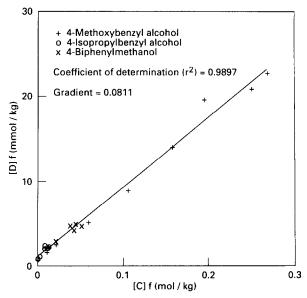


Fig. 4. Relationship between uptake of CI Basic Blue 3 and the concentration of carrier adsorbed by the fibre.

methoxybenzyl alcohol, 4-isopropylbenzyl alcohol and also 4-biphenyl-methanol have been compared to those previously obtained for benzyl alcohol^{9,10} and the three other derivatives of benzyl alcohol.¹¹ Table 1 shows that for the seven carriers under consideration, with the exception of benzyl alcohol, maximum carrier uptake occurred at a concentration in excess of the measured aqueous solubility of the carrier.

A possible explanation for this finding can be offered on the basis that the measured aqueous solubility of the carrier, $C_{\rm aq}$, was compared to the initial concentration of carrier applied to the substrate, $C_{\rm int}$, rather than the actual concentration of carrier in solution in the treatment bath, $C_{\rm s}$. As treatment of the substrate with carrier proceeds, carrier is adsorbed by the fibre up to an amount equal to $C_{\rm f}$, thereby diminishing the actual concentration of carrier in solution (eqn. (1)).

$$C_{\rm s} = C_{\rm int} - C_{\rm f} \tag{1}$$

where C_s is the actual concentration of carrier in solution, C_{int} the initial concentration of carrier applied and C_f the concentration of carrier adsorbed by the fibre.

Since from eqn (1), in the presence of the substrate, the actual concentration of carrier in solution is lower than the concentration of carrier initially applied to the fibre by an amount equal to the concentration of carrier adsorbed by the fibre, it follows that in the presence of fibre, the particular concentration of carrier in solution which corresponds to the measured aqueous solubility of the carrier should be in excess of the carrier's aqueous solubility by an amount equal to the concentration of carrier adsorbed by the fibre (eqn (2)). Thus, as was indeed found (Fig. 1–3), maximum uptake of each of the carriers on to Courtelle S should occur at a

TABLE 1
Comparison of the Measured Aqueous Solubility at 80°C and the Concentration of Carrier in Solution which Gave Maximum Carrier Uptake onto Courtelle S at 80°C

| Carrier | Measured aqueous solubility $(C_{aq}; mol dm^{-3})$ | Concentration giving maximum carrier uptake (C_{so}) ; mol dm ⁻³) | D _c (%) |
|---------------------------|---|---|--------------------|
| Benzyl alcohol | 0.568 | 0.561 | - 1·23 |
| Phenethyl alcohol | 0.267 | 0-294 | 12-4 |
| 3-Phenyl-1-propanol | 0.086 | 0-132 | 53.5 |
| 4-Methylbenzyl alcohol | 0.181 | 0.202 | 11.7 |
| 4-Methoxybenzyl alcohol | 0.400 | 0.496 | 24.0 |
| 4-isopropylbenzyl alcohol | 0.025 | 0.059 | 136.0 |
| 4-Biphenylmethanol | 0.006 | 0.013 | 116.7 |

carrier concentration in solution that is in excess of each carrier's measured aqueous solubility.

$$C_{\rm sol} = C_{\rm aq} + C_{\rm f} \tag{2}$$

where $C_{\rm sol}$ is the carrier concentration in solution that corresponds to the measured aqueous solubility of the carrier and $C_{\rm aq}$ the measured aqueous solubility of the carrier.

From eqn (3) (obtained by rearrangement of eqn (2)), this difference between $C_{\rm sol}$ and $C_{\rm aq}$ is the concentration of carrier adsorbed by the fibre, $C_{\rm f}$, from which it can be assumed that the more hydrophobic the carrier, the greater will be its affinity for the fibre and, consequently, the larger the value of $C_{\rm f}$.

$$C_{\rm f} = C_{\rm sol} - C_{\rm ag} \tag{3}$$

Support for this latter proposal accrues from the $D_{\rm c}$ values displayed in Table 1, which represent the difference between the concentration of carrier that resulted in maximum carrier uptake on to Courtelle S $(C_{\rm sol})$ and the measured aqueous solubility of the carrier $(C_{\rm aq})$ expressed as a percentage of the measured aqueous solubility of the carrier (eqn (4)).

$$D_{c} = \frac{(C_{sol} - C_{aq})}{C_{aq}} \times 100 \tag{4}$$

It is evident from Table 1 and Fig. 5 that the more hydrophobic the carrier

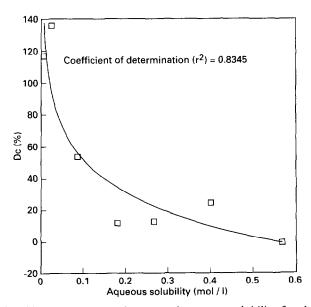


Fig. 5. Relationship between D_c and measured aqueous solubility for the seven carriers.

(i.e. the lower the measured aqueous solubility) the greater is the $D_{\rm c}$ value. Thus, it it can be proposed that the particular concentration of carrier in solution ($[C]_{\rm sol}$) which gave maximum carrier uptake (Table 1 and Figs 1-3) corresponds to the aqueous solubility of the carrier in the presence of fibre and, therefore, that maximum carrier uptake onto Courtelle S relates to the aqueous solubility of the carrier.

Consequently, in view of this proposal, the observed decrease in carrier uptake that occurred at concentrations in excess of the solubility of each carrier (Figs 1-3) can, as previously suggested, 10,11 be attributed to the carrier, at concentrations above its aqueous solubility, being present in the aqueous phase as a saturated solution. This, in turn, results in the carrier having a greater affinity for the saturated, aqueous carrier phase than for the substrate, as a consequence of which the amount of carrier in the fibre decreases as a result of carrier desorbing from the substrate into the saturated carrier solution in the dyebath. Thus, it follows that at concentrations in excess of its aqueous solubility, the carrier may be present in the dyebath as a third (solid) phase. In view of this suggestion, the observed decrease in uptake of CI Basic Blue 3 that occurred at concentrations in excess of the aqueous solubility of each carrier (Figs 1-3) may, as previously suggested 9^{-11} on the basis of the effects of carriers on disperse dyes on polyester fibre, be due to the cationic dye having been restrained within the third (solid) carrier phase in the dyebath.

However, although such dissolution of the cationic dye in carrier present in the dyebath as a third phase may explain the observed decrease in the uptake of CI Basic Blue 3 which occurred at concentrations in excess of the aqueous solubility of each carrier (Figs 1-3), an alternative explanation can be offered in terms of the theory that carriers plasticise the fibre. Previous work by the present authors^{9,10} demonstrated that the maximum extent of T_g reduction of wet Courtelle S tow imparted by benzyl alcohol at 80°C corresponded approximately to the aqueous solubility of the carrier at the particular temperature used (80°C), which, in turn, 10 coincided with the maximum amount of benzyl alcohol adsorbed by the fibre. At concentrations in excess of the aqueous solubility of benzyl alcohol, $T_{\rm g}$ was found to increase with increasing concentration of benzyl alcohol applied, the extent of the increase in T_{g} being proportional to the decrease in uptake of the carrier on to the fibre. It was therefore concluded 10 that the observed increase in $T_{\mathfrak{g}}$ of the substrate that occurred at concentrations in excess of the aqueous solubility of benzyl alcohol was due to a reduction in plasticisation of the fibre, which, in turn, was due to a corresponding decrease in concentration of carrier in the fibre. Also, it was found that uptake of CI Basic Blue 3 onto Courtelle S coincided with the extent of plasticisation of the fibre imparted by benzyl alcohol, insofar as a plot of dye

uptake versus carrier concentration was virtually superimposable on that of the variation of $T_{\rm g}$ with carrier concentration; it was thus concluded that the decrease in dye uptake that occurred at concentrations in excess of the aqueous solubility of benzyl alcohol was primarily due to a reduction in the extent of fibre plasticisation.

Support for this view was provided¹¹ by the findings that in the presence of 3-phenyl-1-propanol, 4-methylbenzyl alcohol and phenethyl alcohol, the maximum extent of uptake of CI Basic Blue 3 onto Courtelle S coincided with the maximum extent of adsorption of each of the three carriers used; similarly, Figs 1–3 clearly show that the maximum extent of uptake of CI Basic Blue 3 coincided with the maximum extent of uptake of the three carriers under consideration. Figure 6 shows that a linear relationship was obtained between maximum uptake of CI Basic Blue 3 and maximum carrier uptake for each of the seven carriers under consideration. Thus, it is proposed that the maxima in dye uptake obtained for 4-methoxybenzyl alcohol, 4-isopropylbenzyl alcohol and 4-biphenylmethanol (Figs 1–3) corrrespond to the maximum extent of plasticisation of the fibre, and that the observed decrease in dye uptake that occurred for an increase in carrier concentration above the aqueous solubility of each carrier can be attributed to a corresponding reduction in plasticisation of the substrate.

According to the plasticisation theory of carrier dyeing, the extent of plasticisation of Courtelle S, and, hence, the extent to which the uptake of CI

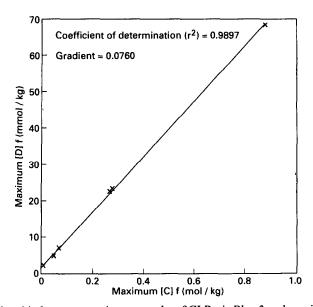


Fig. 6. Relationship between maximum uptake of CI Basic Blue 3 and maximum uptake of each of the seven carriers.

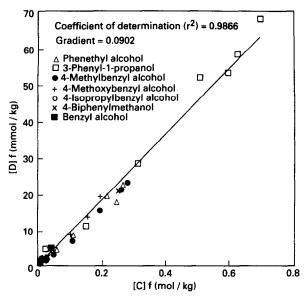


Fig. 7. Relationship between uptake of CI Basic Blue 3 and uptake of each of the seven carriers.

Basic Blue 3 was enhanced, should be related to the concentration of carrier (diluent) adsorbed by the substrate. The results shown in Fig. 7 confirm this, in that all the points for each of the seven carriers lie on a straight line and, therefore, for each carrier, irrespective of chemical constitution, the extent of carrier action increases with increasing concentration of carrier within the fibre.

The Solubility Parameter Concept was previously employed¹¹ to demonstrate that the maximum extent of uptake of benzyl alcohol and also 3-phenyl-1-propanol, 4-methylbenzyl alcohol and phenethyl alcohol onto Courtelle S two was related to the δ_a value of the carrier. In this context, Figs 8-10 show the variation of maximum uptake of each of the seven carriers with the total (δ_1) , association (δ_2) and dispersion (δ_3) solubility parameters, respectively. Although, for each of the three solubility parameters considered, maximum carrier uptake increased as the respective solubility parameter of the carriers approached that of the fibre, the highest coincidence of all points to each of the three curves shown (as given by the coefficient of determinations displayed in Figs 8-10) was found for the plot of maximum carrier uptake as a function of the δ_a values of the seven carriers, thus confirming both the earlier finding¹¹ that maximum carrier uptake is related to the association solubility parameter, and also the proposal of Ingamells et al. 12,13 that polar forces are responsible for carrier-acrylic interaction.

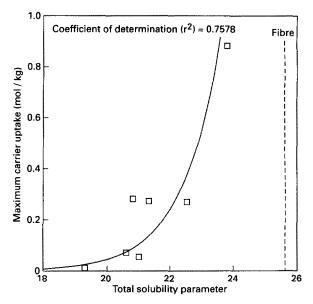


Fig. 8. Relationship between maximum carrier uptake and total solubility parameter for the seven carriers.

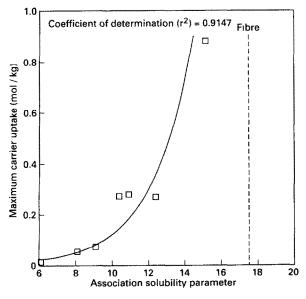


Fig. 9. Relationship between maximum carrier uptake and association solubility parameter for the seven carriers.

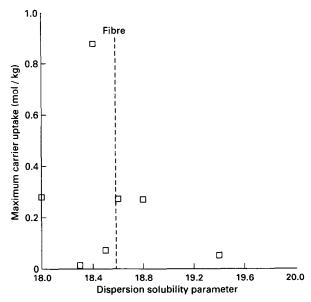


Fig. 10. Relationship between maximum carrier uptake and dispersion solubility parameter for the seven carriers.

However, as previously suggested, 11 a relationship can be considered to exist between the aqueous solubility and the δ_a value of the carrier; as water is highly polar, the carrier-water interaction (dissolution) should increase with increasing magnitude of the δ_a value of the carrier. Indeed, Fig. 11 shows that the measured aqueous solubility of the seven carriers under consideration increased with increasing δ_a values. This finding therefore supports the earlier proposal that maximum carrier uptake is related to the aqueous solubility of the carrier.

According to the plasticisation theory of carrier action, in order for a carrier to function, it must be adsorbed by the fibre and, therefore, the efficacy of a given carrier will depend upon the substantivity and diffusional characteristics of the carrier. In this context, if it is considered that the solubility parameter concept represents, essentially, carrier—acrylic fibre substantivity, the molecular volume of a carrier can be considered as being an approximate indication of the diffusional character of the carrier within the substrate. Table 2 and Fig. 12 show that maximum uptake of each of the seven carriers was clearly related to the molecular volume of each carrier, as evidenced by the high coefficient of determination obtained for the plot of maximum carrier uptake versus molecular volume. A possible explanation of this finding can be forwarded on the basis of the free volume model of diffusion of solutes within acrylic fibres. In order for a solute molecule, in this case a carrier, to diffuse within the substrate, sufficient free volume within the

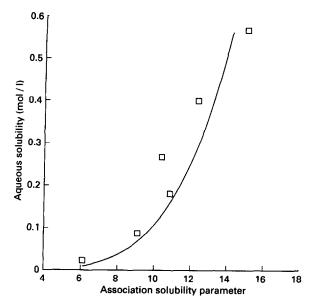


Fig. 11. Relationship between measured aqueous solubility and association solubility parameter for each of the seven carriers.

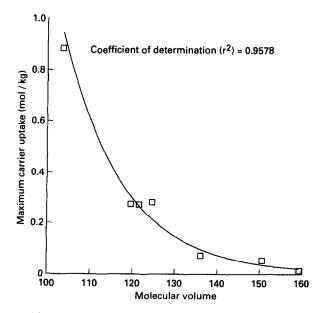


Fig. 12. Relationship between maximum carrier uptake and molecular volume for the seven carriers.

Data for Carriers and Acrylic

| | Aqueous solubility | Maximum carrier | Maximum dye | Solul (M) | Solubility parameter (MPa ^{1/2} at 25°C) | neter 'C) | Molecular volume* |
|---------------------------|---|--------------------|-------------------------|--------------|--|----------------|---|
| | $(M dm^{-3})$ | $(M kg^{-1})$ | $upiake$ $(mM kg^{-1})$ | ρ | Pφ | δ _a | |
| Benzyl alcohol | 0.568 | 6880 | 90.89 | 23.84 | 15.1" | 18.4" | 103-8 |
| Phenethyl alcohol | 0.267 | 0.265 | 22:76 | 22.16 | 12·0° | 18.6^{d} | 119.8 |
| 3-Phenyl-1-propanol | 980-0 | 0.071 | 7.28 | 21.3^{b} | 10.6^{c} | 18.5^{d} | 136.5 |
| 4-Methylbenzyl alcohol | 0.181 | 0.279 | 23·29 | 21.6^{b} | 11.9° | 18.04 | 124.9 |
| 4-Methoxybenzyl alcohol | 0.400 | 0.269 | 22:69 | 22.5b | 12.46 | 18.84 | 121.9 |
| 4-Isopropylbenzyl alcohol | 0.025 | 0-013 | 2.48 | 19.3^{b} | 9.10 | 19.44 | 159.8 |
| 4-Biphenylmethanol | 900-0 | 0.054 | 5.03 | 21.0^{b} | 8.10 | 18.34 | 151.0 |
| Acrylic | *************************************** | MARAGEMENT | ı | 25.6" | 17.6^{a} | 47.8 | *************************************** |

^a From Ref. 19.

^b Calculated from boiling point and molecular volume.¹⁹ ^c Calculated from $\delta_a^2 = \delta_t^2 - \delta_d^2$.
^d Calculated from refractive index.¹⁵
^e Calculated from $V_m = M_t/\rho$.

fibre must be available; the extent of carrier diffusion will therefore depend upon carrier—fibre substantivity, which will be determined by factors such as pH, temperature, etc., as well as the carrier's diffusional characteristics, which will be determined by the molecular size or volume of the carrier. Thus, it can be proposed that for given pH, temperature, etc., the smaller the molecular volume of the carrier the greater will be the extent of carrier diffusion within the substrate; this carrier diffusion within the fibre will, in turn, result in plasticisation of the substrate and thus increased free volume, which will lead to a greater extent of carrier diffusion and thus a greater extent of plasticisation. Consequently, in terms of the results obtained (Table 2 and Fig. 12) it can be suggested that of seven carriers used, that with the smallest molecular volume, namely benzyl alcohol, should exhibit the greatest uptake on to the fibre and thus exert greatest plasticising (i.e. carrier) action, as indeed was observed.

An alternative explanation for the finding that maximum carrier uptake was related to the molecular volume of the carrier may be given if it is considered that, in general, the aqueous solubility of a solute molecule will decrease with increasing molecular volume. This proposition gains support from the plot of the measured aqueous solubility of each carrier as a function of molecular volume (Fig. 13) and thus can be considered to further support the suggestion that maximum carrier uptake is related to the aqueous solubility of the carrier.

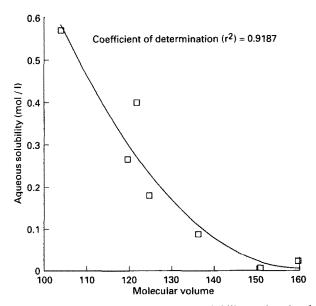


Fig. 13. Relationship between measured aqueous solubility and molecular volume for the seven carriers.

4 CONCLUSIONS

The observation that the extent to which uptake of CI Basic Blue 3 on Courtelle S was enhanced by the seven carriers was proportional to the amount of carrier adsorbed by the fibre indicates that each carrier acts as a diluent of the substrate, the extent of carrier action (i.e. plasticisation) increasing with increasing concentration of carrier within the fibre. The results obtained suggest that the amount of carrier which can be adsorbed by the fibre and thus the extent of carrier action imparted to dye uptake, are related to the aqueous solubility of the carrier. This is not surprising in view of the well-known findings that carrier adsorption on to acrylic^{1,14} and other hydrophobic fibres^{4,15-18} occurs via a Nernst mechanism, as observed for the adsorption of disperse dyes on to such fibres, for which it is widely accepted that dye adsorption occurs only from aqueous solution.

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REFERENCES

- 1. Kim, J. P., PhD thesis, Leeds University, 1990.
- 2. Burkinshaw, S. M. & Kim, J. P., J. Korean Fiber Soc., 28 (1991) 549.
- 3. Kaushik, R. C. D. & Deshpande, S. D., Indian J. Text. Res., 14 (1989) 125.
- 4. Kaushik, R. C. D. & Deshpande, S. D., Indian J. Text. Res., 14 (1989) 130.
- Rawicz, F. M., Cates, D. M. & Rutherford, H. A., Am. Dyest. Rep., 66 (1968) 284.
- McGregor, R., Peters, R. H. & Ramachandran, C. R., J. Soc. Dyers Colour., 84 (1968) 9.
- 7. Balmforth, D., Bowers, C. A., Bullington, J. W., Guion, T. H. & Roberts, T. S., *J. Soc. Dyers Colour.*, **82** (1966) 405.
- 8. Ingamells, W. C. & Narasiham, K. V., J. Soc. Dyers Colour., 93 (1977) 306.
- 9. Aitken, D., Burkinshaw, S. M., Catherall, J., Cox, R. & Price, D. M., J. Appl. Polym. Sci., Appl. Poly. Sympos., 47 (1991) 271.
- 10. Aitken, D., Burkinshaw, S. M. & Price, D., Dyes and Pigments, 18 (1992) 23.
- 11. Aitken, D. & Burkinshaw, S. M., J. Soc. Dyers Colour., 108 (1992) 219.
- 12. Gur-Arieh, Z., Ingamells, W. & Peters, R. H., J. Soc. Dyers Colour., 92 (1976) 332.
- 13. Ingamells, W. C. & Yabani, A., J. Soc. Dyers Colour., 93 (1977) 417.
- 14. Tokaoka, A. & Aki, M., Sen-i Gakkaishi, 21 (1965) 425, 432, 437.
- 15. Koenhen, D. M. & Smolders, C. A., J. Appl. Polym. Sci., 19 (1975) 1163.

- 16. Salvin, V. S., Am. Dyest. Rep., 48 (1959) 23.
- 17. Jin, C. R. & Cates, D. M., Amer. Dyest. Rep., 53 (1964) 64.
- 18. Fortress, F. & Salvin, V. S., Text. Res. J., 28 (1958) 1009.
 19. Barton, A. H. F., In CRC Handbook of Solubility Parameters and Other Cohesion Parameters. CRC Press, Boca Raton, FL, 1983.