Technology Section

PARTICLE SIZE OF DISPERSE DYES BY PARTITION CO-EFFICIENT MEASUREMENT

Shazia Akbar, Ali Mohammad, Shahina Waheed*, M. Farooq* and Badruddin*

Institute of Chemistry, University of the Punjab, Quaid-e-Azam Campus, Lahore-54590, Pakistan

Disperse Red 1 and disperse Orange 25 were prepared and their IR spectra were recorded. The partition ratio in aqueous suspension of water and chloroform for these dyes was determined at various milling time intervals. A gradual increase in (water/CHCl$_3$) ratio indicated the progress of particle size reduction. The quality of dispersion was further confirmed by dyeing cellulose acetate fabric with these dyes as they gave uniform dyeing with good build up and no specks on the dyed fabrics were observed.

Key words: Disperse dyes. Dispersion and particle size.

Introduction

Almost all azo dyes are prepared by conventional diazo-tization and coupling reactions [1-2], the mechanisms and limitations of which are now widely known. Disperse dyes have very low solubility in water and therefore, are applied from an aqueous dispersion. The quality of dispersion has a pronounced influence on the quality of disperse dyes. The eveness of dyeing depends [3- 5] on the fineness of the dye particles as wel as on the stability of the dispersion. The finer the particle, the better the dispersion [6-8]. The well known methods of particle size determination involve the Coulter counter [9], disc centrifuge [10], gas adsorption isotherms or sedimentation techniques [11] etc. All these methods require much elaborate equipment and are time consuming. Recently another approach has been described in which the partition coefficient of the aqueous dye dispersion with respect to an immiscible organic solvent (in which the dye is soluble) has been related to the dispersion quality and particle fineness. This rapid method [12] is simple and does not require costly apparatus. The value of the partition coefficient provides information about the dispersibility of the dye. The present work describes the determination of the partition coefficient of different dyes in water and a water immiscible solvent. The objective was to verify and further refine the relationship of dispersibility with the partition coefficient values.

Experimental

Instruments. Infrared spectra were recorded on a Hitachi 270-30 spectrophotometer. Melting points were taken on hot stage polarization microscope model MRK. A dyeing machine (Roaches) was used for dyeing cellulose acetate fabric at 130°.

Intermediates and solvents. Commercial grade chemicals and intermediates were used for the preparation of azo dyes.

* PCSIR Laboratories Complex, Lahore-54600, Pakistan.

Distilled acetone and chloroform were used for spectroscopic and partition coefficient studies.

Preparation of disperse Red 1 dye colour index number (11110)[1] [13]. Diazotization. To a beaker added 3.1 g of para nitroaniline (0.022 moles) and 11 cm^3 HCl (12° Be) to make a uniform mixture. Then added 50 cm^3 of water, cooled the mixture to 10° and then added 1.5 g of sodium nitrite (0.022 mole) with vigorous stirring and keeping the temp. at 10° or below. The excess of sodium nitrite was destroyed with sulphamic acid.

To a beaker (500 cm) added 9.3 g 2(N-ethyl anilino) ethanol (0.026 mole) and 10 cm^3 HCl (12° Be). The contents of the beaker were stirred for 2 hr. at room temperature till a homogenous mixture was obtained. With vigorous stirring, added crushed ice, 100 cm^3 of water and 0.5 g of dispersing agent Tamol NNOK (BASF). When the temperature reached 10°, the diazotized solution was added to this coupling solution so that the temperature remained between 10-15°. After the addition was completed, the stirring was continued for a further 30 min. and then added (14%) solution of sodium bicarbonate (150 cm^3) to adjust the pH of the reaction mixture at 3. Keeping the temperature at 10° stirring was continued for 2 hr. and the presence of diazo components was checked with 1-naphthylamine-3,6,8-trisulfonic acid solution. At the end, the contents were diluted with 50 cm^3 of water and filtered. The residue was washed thoroughly with water for 2 hr. The cake was removed and dried at 60-70° (yield 6.7 g 82%).

The recrystallization from acetone yielded rhombic dark crystals m.p. 158-160° (lit. m.p. 160°) disperse orange 25 (colour index number 11227)[2].

The diazotisation was done as for disperse Red 1.

Coupling reactions. To a beaker was added 4.4 g of 2(N-ethyl anilino) ethyl cyanide (0.0252 mole) and 25 cm^3 HCl (12° Be) and followed the procedure as described for disperse Red-1. The yield of the dye prepared was 6.84g (95%). The re-

crystallization from acetone gave crystals with m.p. 174-176° (lit. m.p. 176°).

Spectrophotometric studies of disperse dyes. The absorption spectra of disperse Red 1 and disperse Orange 25 were measured in the visible range on the UV/visible spectrophotometer. The results are shown in Fig. 1 for disperse Red 1 and Fig. 2 for disperse Orange 25 which have maximum absorbances at 488 nm and 460 nm, respectively.

Plotting of standard graphs of dyes. Dissolved 0.1 g of each dye in 50 cm³ of acetone. Appropriate dilutions were made for each dye solution and their absorbances were determined. The plots were drawn showing relationship between concentration of dye in g/l and the determined absorbance. A linear relationship is shown in Fig. 3 for Red 1 and Orange 25 as expected from the Beer Lambert law.

Infrared spectroscopy of disperse dyes. The IR spectrum of disperse Red 1 showed absorption bands at wave number (cm) in Nujol. 3268 (OH); 1143 (C-O stretching), 1605, 1597, 1518, 1467 (aromatic ring stretching), 1383 (N-O asymmetric and symmetric stretching) 861 (P-substituted benzene ring).

The IR spectrum of disperse Orange 25 showed bands at wave number (cm) in Nujol 2250 (C = N stretching), 1605, 1521, 1467 (aromatic ring stretching); 1521, 1380 (N-O asymmetric and symmetric) 861 (P. subst. benzene ring).

Determination of partition coefficient of disperse Red 1 and disperse Orange 25. disperse Red 1. The dried sample of disperse Red 1 with the dispersing agent (Tamol NNOK) in the ratio 60:40 was pasted in the presence of small amount of water to make it more fluid. The paste was ground in a ball mill for 30 hr. 1 cm³ of the paste was drawn at 5 hr. interval and added into 100 cm³ water. 20 cm³ of this aqueous dispersion was taken in a separatory funnel and extracted with chloroform (20 cm³) by slowly rotating for 5 min. The chloroform and aqueous layers were separated.

The Table 1 shows absorbance of disperse Red 1 at 488 nm extracted from the aqueous and chloroform layers after grinding intervals of 5, 10, 15, 20, 25 and 30 hr. From the Beer-Lambert standard graph 1, the value of the partition coefficient $K = C_w/C_s$ was calculated and the graph was plotted between K and time of milling (Fig. 4).

Disperse Orange 25. By following the procedure as above for disperse Red 1, the absorbance of dye at 460 nm in water and solvent system was determined and concentration was measured from the absorption of the standard graph 1 and given Table 2. The partition ratio K was then plotted against time of milling (Fig. 4).

Dyeing of polyester fabrics. Weighed disperse dye (1.0 g) was placed in a mortar. Added few drops of DMF and 0.5 g Tamol NNOK (BASF). This mixture was thoroughly mixed to a homogenous paste and added 90 cm³ water, again stirred to make the solution. It was filtered through cotton plug to remove any large foreign particle. It was washed with 10 cm³ of water. The final dye solution was made upto 100 cm³ in a volumetric flask.
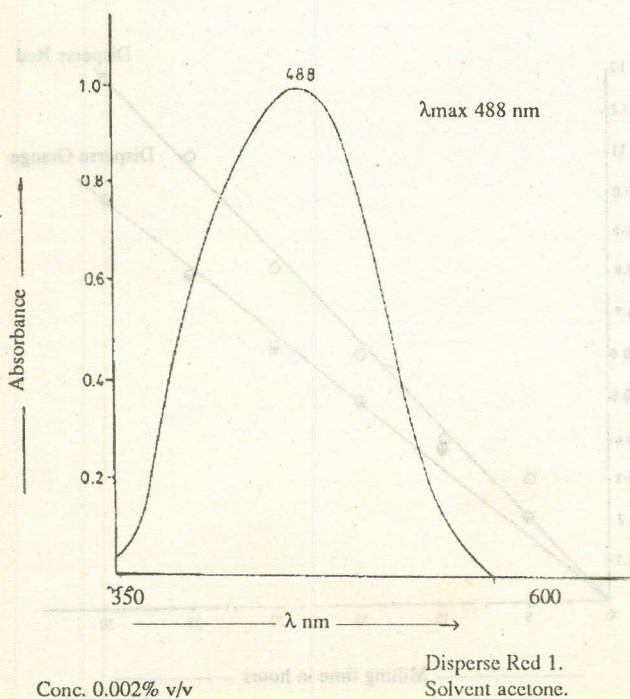

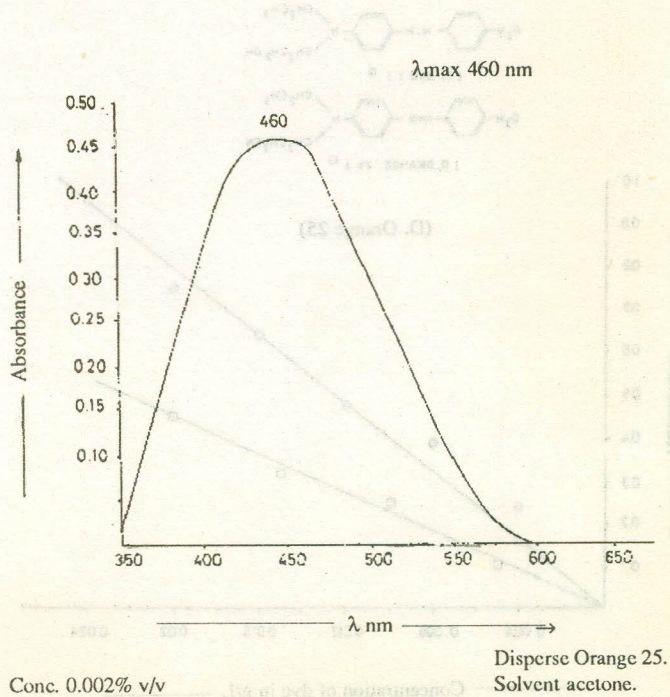Disperse Red 1.
Solvent acetone.
Conc. 0.002% v/v

Fig. 1.

λmax 460 nm

Disperse Orange 25.
Solvent acetone.
Conc. 0.002% v/v

Fig. 2.

TABLE 1. PARTITION OF DISPERS RED 1 AT DIFFERENT INTERVALS OF TIME.

Milling in time hr.	Absorbance at 488nm		Conc. in g/l from graph in diluted solution		Final conc. of dye after considering dil. factor		$K=C_w/C_s$
	Aqueous layer	Solvent layer	Aqueous layer	Solvent layer	Water (C_w)	Solvent (C_s)	
5	0.070	0.537	0.003	0.024	0.0750	0.235	0.032
10	0.27	0.410	0.012	0.0176	0.300	1.76	0.170
15	0.303	0.350	0.0135	0.0155	0.340	1.55	0.220
20	0.377	0.300	0.017	0.0135	0.425	1.35	0.315
25	0.390	0.212	0.018	0.0096	0.4500	0.96	0.470
30	0.412	0.204	0.0185	0.0090	0.4625	0.90	0.513

TABLE 2. PARTITION OF DISPERS ORANGE 25 AT DIFFERENT INTERVALS OF TIME.

| Milling in time hr.	Absorbance at 460nm		Conc. in g/l from graph in diluted solution		Final conc. of dye after considering dil. factor		$K=C_w/C_s$
	Aqueous layer	Solvent layer	Aqueous layer	Solvent layer	Water (C_w)	Solvent (C_s)	
5	0.080	0.420	0.0018	0.0106	0.045	1.060	0.042
10	0.106	0.302	0.0024	0.0076	0.061	0.760	0.079
15	0.142	0.200	0.0036	0.0050	0.090	0.50	0.180
20	0.184	0.176	0.0044	0.0044	0.112	0.44	0.250
25	0.222	0.150	0.0056	0.0036	0.143	0.36	0.384
30	0.260	0.130	0.0066	0.0030	0.165	0.30	0.550
35	0.300	0.102	0.0072	0.0024	0.180	0.24	0.75
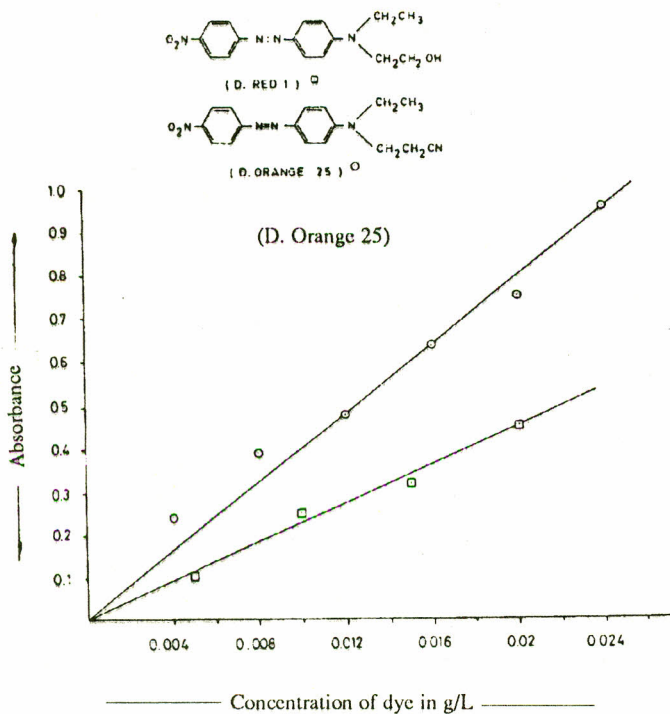
Fig. 3.
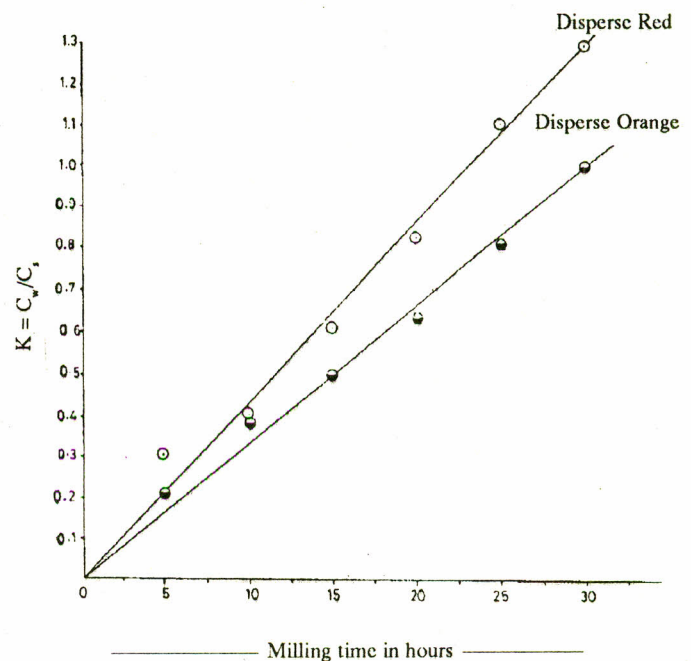
Fig. 4.

In order to dye the polyester fabric, the following formula is used to calculate the volume of stock solution required for 1% or 2% depth.

No. of cm stock solution required = W x P/C

where W = Weight in g of sample to be dyed, P = Percentage of dye to be used (expressed as weight of fabric), C = Concen-tration of the dye in the volume taken from the stock solution.

Results and Discussion

The disperse dyes are marketed in the form of a fine powder containing the dispersing agents which make good dispersion in aqueous media. During dyeing, more dispersing agents are added in the dyebath to stablise the dispersion and to get better dyeing results.

In the laboratory, the dyes are generally dispersed by grinding in vibro energy mill or ball or sand mills in the presence of suitable dispersing agents. In these studies the small laboratory ball mill was used for milling disperse Red 1 and disperse Orange 25.

No information was available for the laboratory scale dispersion of these dyes in the literature, except some examples of the measurement of particle size of pigments and disperse dyes such as Disperse Yellow 3 by microscopy, sedimentation and conductivity methods. Kissa [12] has studied the dispersibility of disperse yellow 1, disperse Orange 2 dyes and pigments by a partitioning method in water and chloroform system and correlated the partition coefficient with the particle size. The partitioning method was used in the present study as it was more convenient and did not need sophisticated instruments.

The method suggested by Kissa [12] gives an idea of particle size and the dispersion quality. In case of an ideal dispersion, the quantity of the dye extracted should be almost negligible and the ratio C_w/C_s should approach infinity. As can be seen from the Table and graphs of disperse Red 1 and disperse Orange 25, the ratio C_w/C_s increases rapidly as the time of grinding increases. The quantity extracted in the solvent goes on decreasing because the smaller particles adsorb the dispersing agent which protects the particles from passing from aqueous phase to the organic phase. In both the

dyes, the straight lines were obtained by plotting grinding time against partition coefficients. The graph of partition coefficient C_w/C_s against grinding time shows that the slope in case of disperse Red 1 is higher than that of disperse Orange 25. This can be attributed to the presence of a polar 2-hydroxyethyl group in disperse Red 1 which has more affinity towards adsorbing the dispersant on its surface and hence shows better dispersion quality than the 2-cyanoethyl group in disperse Orange 25.

Dyeing on polyester. The disperse dyes were also applied on the polyester fibre in pressure dyeing machine. The dyeing was of uniform shade and no specks or spots were observed. This further confirmed the expected results that the grinding with the dispersant gave good stable dispersion.

From the above grinding, it has been concluded that the partition coefficient measurement is quite a rapid and sure method of assessing the dispersion quality and indirectly it will give an idea of fineness of the ground disperse dyes. This method is very convenient to follow the course of grinding where the manufacturing of these dyes is being done.

References

1. BIOS Report No. 961, 79; BIOS 1548, 202.
2. K. Venkataraman, *The Analytical Chemistry of Synthetic Dyes* (John Wiley and Sons, New York, 1977), pp. 370.
3. A.G. Green and C. Saunders, J.S.D.C., **32**, 10 (1923).
4. R.K. Fourness, J.S.D.C., **69**, 121 (1953).
5. R.K. Rourness, J.S.D.C., **90**, 15 (1974).
6. P. Richter and M. Vescia, Melliand Textilberichte, **46**, 621 (1965).
7. D. Peterson and A.R. Hannan, J.S.D.C., **79**, 192 (1963).
8. C.P. Baker and J.F. Vozzella, Official Digest, **22**, 311 (1950).
9. H.E. Kubitschek, Research (London), **13**, 128 (1963); W.H. Coulter, Proceedings of the National Electronics Conference, **12**, 1034 (1956).
10. E. Atherton and D. Tough, J.S.D.C., **81**, 624 (1955).
11. J.D. Hildreth and D. Patterson, J.S.D.C., **80**, 474 (1964).
12. Erik Kissa, Textile Res. J., Feb., 66 (1989).
13. *The Colour Index* (Society of Dyers and Colourists, Bradford, U.K., 1971).