Dyes and Pigments, Vol. 38, Nos 1–3, pp. 173–180, 1998
© 1998 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
PII: S0143-7208(97)00077-6 0143-7208/98 $19.00+0.00

Dispersability of Organic Pigments

C. Daescu

University Politehnica of Timisoara, Faculty of Industrial Chemistry, Piata Victoriei Nr 2,
1900 Timisoara, Romania

(Received 16 June 1997; accepted 28 July 1997)

ABSTRACT

Dispersability of some vat dyes and azo pigments is defined, measured and correlated with the calculated hydrophobicity. Aggregation degree in aqueous dispersions of these pigments stabilized by dispersants is also determined.

© *1998 Elsevier Science Ltd. All rights reserved*

Keywords: dispersability, organic pigments, hydrophobicity.

INTRODUCTION

Disperse and vat dyes are especially hydrophobic (Ryophilic) pigments. Their application from aqueous baths requires the final processing (conditioning) of a great amount of dispersants. Their purpose is to prevent the aggregation of dye particles resulting from dry or wet micronization in ball-mills; with aggregation the specific surface decreases. This surface is responsible for the transfer of the dye from the solid phase to the aqueous bath (k_1), the maintenance of its concentration in the bath (k_2) and the transport to the boundary layer from the fiber surface (k_3) [1]:

$$[\mathrm{dye}]_{\mathrm{solid}} \overset{k_1}{\rightleftharpoons} [\mathrm{dye}]_{\mathrm{solution}} \overset{k_2}{\rightleftharpoons} [\mathrm{dye}]_{\mathrm{surface}} \overset{k_3}{\rightleftharpoons} [\mathrm{dye}]_{\mathrm{ads}} \overset{k_4}{\rightleftharpoons} [\mathrm{dye}]_{\mathrm{diff}}$$

The rate of dyeing can depend on each of the four steps, of which the dispersants control the first three. As a result, the mass ratios dye/dispersant (K) used to obtain commercial forms of vat and disperse dyes are greater than the unit (K > 1). The ratio value varies from 1 for C.I. Disperse Red 32 to 2.25 for C.I. Disperse Brown 56 and even more [2–5]. The baths of vat dyes usually contain ca 1 g litre^{-1} and dyeing with disperse dyes in presence of carriers in pad-roll system requires up to 5 g litre^{-1}.

The purpose of this paper is to determine both the minimum amount of dispersant required to prevent the aggregation of dispersed dye, and the aggregation degree of the dye in aqueous media in presence of dispersants.

EXPERIMENTAL

The soluble forms of a commercial series of vat dyes (Indigosol, Anthrasol, Hellasol) were hydrolysed–oxidised in presence of increasing amounts of dispersant. There properties are shown in Table 1. The absorption maximum (λ_{max}) and specific extinction (ε') correspond to those of dispersions with a great excess of dispersant.

The syntheses of azo pigments in presence of dispersant were performed under controlled conditions. Thus, in volumetric flask of 100 ml were placed known and increasing amounts, in the range 0.2÷10 ml, of 5 g litre^{-1} aqueous solution of Dispersil WS, then 0.1 ml 0.1 M coupling solution in alkaline medium (pH = 11–12) and, under stirring, 0.1 ml 0.1M solution of freshly prepared diazonium salt. The mixture thus obtained was kept 2 h, completed to the mark with distilled water and its extinction measured with a Specord UV-VIS (C. Zeiss, Jena) spectrophotometer. From the plot of dispersion extinction vs dispersant concentration, an intersection of two straight lines was observed. The abscissa of their intersection affords the calculation of K*; e.g. the data represented in Fig. 1 were obtained for the pigment *m*-chloroaniline→Naphtol AS at 10^{-4}M concentration: $c_D^* = 0.033$ g litre^{-1}

TABLE 1
Properties of the Solubilised Vat Dyes Used

Dye	*C.I.*	*M*	λ_{max} *(nm)*	$\varepsilon'(l.g^{-1})$
Anthrasol gold gelb IGK	59,101	536	435	11.2
Anthrasol gold gelb IRK	59,106	694	450	6.53
Selenco violet I4R	60,011	729	522	9.00
Hellasol grün IB	69,501	755	650	5.40
Anthrasol blau IBC	69,826	919	605	5.37
Anthrasol braun IBR	70,801	1256	416	2.68
Indigosol Rosa IR	73,361	533	520	8.13
Indigosol grau IBL	73,671	532	595	4.44

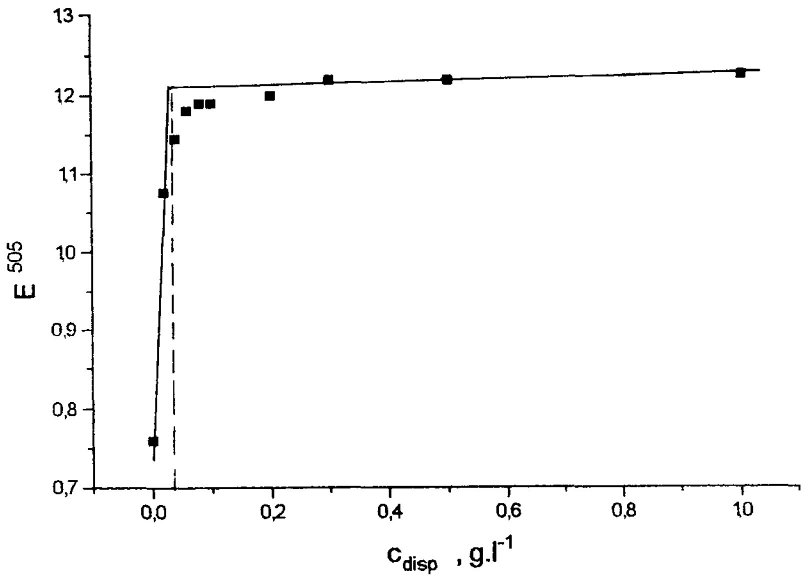

Fig. 1. Extinctions of the pigment *m*-cloroaniline→Naphtol AS vs dispersant concentration.

RESULTS AND DISCUSSIONS

In the bath, hydrophobic dyes probably exist in the form of complexes consisting of many dye and dispersant molecules linked together by van de Waals hydrophobic–hydrophobic interactions.

Mechanical grinding decreases the size of the particles down to about 1 μm which is greater by a three order magnitude of molecular dimensions. Preparation of a molecular dimension size dispersion has been achieved by sythesis of some azo pigments [6], particularly by hydrolysis and oxidation of the sulfuric esters of the reduced forms of vat dyes [7] in the presence of disperants. The 'in situ' dyes thus obtained aggregated in absence of dispersants but remained in quasi-molecular dispersion in their presence.

Using spectrophotometric methods, one can determine the critical amount of dyes (K*) (in grams), that can be kept in dispersion by 1 g of a standard dispersant (Dispersil WS, Colorom, Romania or Reax, West Vaco, USA). One can consider as dye 'dispersability' ($\mathcal{D}$) this amount expressed in mmoles:

$$\mathcal{D} = 10^3 K^*/M_{dye}$$

When a well-defined molecular mass dispersant is used (e.g. Dispersil WS, dinaphthylmethane–disulphonic acid disodium salt) the aggregation degree of the dye ($\mathcal{A}$) from the complex dye-dispersant can be calculated as the molar ratio of the two components:

$$\mathcal{A} = [\text{dye}]/[\text{dispersant}] = K^{*}M_{\text{dispersant}}/M_{\text{dye}}$$

The two measures are proportional. For the pigment *m*-chloroaniline→Naphtol AS (Fig. 1) one can calculate: $K^{*}=1.217$; $\mathcal{D}=3.031$; $\mathcal{A}=1.43$.

Attempts to correlate the dispersability of vat dyes with their chemical structure (number of heavy atoms, molecular mass, number of rings) or with their physical properties (λ_{max}, ε_{max}) has led to non-meaningful results.

It is easy to accept that the association of molecules within the complex is achieved through hydrophobic–hydrophobic interactions, where the hydrophobic parts of both dye and dispersant are involved. It could be expected that $\mathcal{D}$ would depend on the hydrophobility of the dye. Hydrophobicity can be quantitatively characterized by the coefficient of partition (P) in a system of two immiscibile hydrophobic–hydrophilic solvents, as expressed by the Nerst law: $P=[\text{dye}]_{\text{lyophilic}}$ / $[\text{dye}]_{\text{hydrophilic}}$. The logarithm of P (log P) is known as π Hansch, and can be either determined experimentally or calculated from group contributions [8]. The Rekker method calculates log P for the system n-octyl alcohol/water.

For some polycyclocetonic dyes these values have been determined, and are shown in Table 2. Both dispersability and aggregation increase quite

TABLE 2
Dispersability and Aggregation of Some Vat Dye

	Dispersal WS		*Reax*			
Dye	K^{*} $g_{dye}\,g_{disp}^{-1}$	$\mathcal{D}_{\mathcal{D}}$ $mmol_{dye}\,g_{disp}^{-1}$	K^{*} $g_{dye}\,g_{disp}^{-1}$	$\mathcal{D}_{\mathcal{R}}$ $mmol_{dye}\,l\,g_{disp}^{-1}$	*log P* mol_{dye}^{-1}	$\mathcal{A}$ mol_{disp}^{-1}
C.I. Vat Yellow 4 C.I.59,100	5.52	10.04	4.44	8.28	5.16	4.90
C.I. Vat Orange 1 C.I.59,105	12.50	18.01	11.50	16.57	7.03	8.57
C.I. Vat Violet 1 C.I.60,010	1.25	1.71	2.00	2.74	8.90	0.816
C.I. Vat Green 3 C.I.69,500	6.76	8.95	6.02	7.97	5.34	4.26
C.I. Vat Blue 6 C.I.69,825	5.35	5.82	3.40	3.70	4.75	2.77
C.I. Vat Brown 1 C.I.70,800	9.20	7.32	7.25	5.77	5.18	3.49
C.I. Vat Red 1 C.I.73,360	6.87	12.9	5.90	11.22	6.57	6.14
C.I. Vat Black 1 C.I.73,670	7.83	14.7	7.15	13.4	5.90	7.00

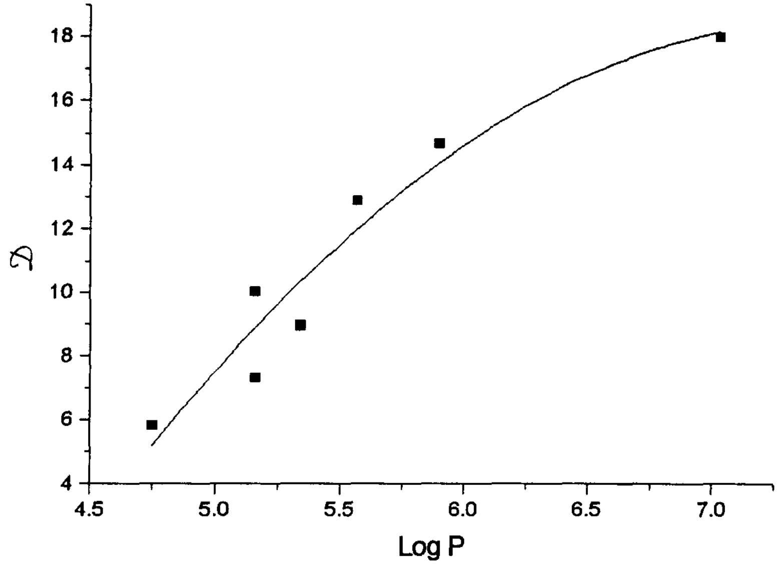

Fig. 2. Dispersability of vat dyes vs hydrophobicity.

coherently with the increase of dye hydrophobicity (Fig. 2). The aggregation degree is about 3–8 molecules of dyes molecule of dispersant^{-1}. An exception is with dichloro-dibenzanthrone (C.I. Vat Violet 1), which forms a complex of about 1:1, probably because of its strongly compact condensed structure, making it a singular case.

An attempt to correlate dispersability and aggregation with calculated hydrophobicity is troublesome because of the insufficiency of data and its great dispersion. Except for C.I. Vat Violet 1, eqns (1) and (2) for Dispersil WS and, respectively, eqn (3) for Reax result. As expected, the precision of the mathematical model is rather poor. Both the values and the form of correlation eqns depend on the nature of the dispersant used

$$\mathcal{D}_{\mathrm{D}} = 40 - 162/\log \mathrm{P} \quad n = 7;\ r = 0.926;\ s = 0.426;\ F = 30.1 \tag{1}$$

$$\mathcal{A}_{\mathrm{D}} = 19 - 76.5/\log \mathrm{P} \quad n = 7;\ r = 0.922;\ s = 0.87;\ F = 28.3 \tag{2}$$

$$\mathcal{D}_{\mathrm{R}} = 39.4 - 167/\log \mathrm{P} \quad n = 7;\ r = 0.925;\ s = 0.85;\ F = 29.6 \tag{3}$$

where n-number of data, r-correlation coefficient, s-standard deviation and F-Fisher test. The value 1/K* represents the minimum amount of dispersant required to obtain a quasi-molecular dispersion. It varies in the limits of 0.8÷0.08 grams of Dispersil WS gram of dye^{-1}, or 0.5÷0.05 grams of Reax gram of dye^{-1}. In commercial dispersions, which are much more coarser, it is expectable to need even a smaller amount, since the aggregation degree is superior.

The results obtained for some simple azo pigments are given in Table 3. These pigments are similar to many disperse azo dyes. Here again, dispersability increases, as expected, with increase of hydrophobicity. The much more polar structure of azo pigments leads to an inferior dispersability than that of the vat dyes, and an aggregation degree of about 1÷2. It follows that the aggregated dye-dispersant complexes thus obtained are of the type 1:1 for the simple monoazo dyes with 2-naphthol and, respectively, 2:1 and 3:2 for disazo dyes and chloroaniline derivatives.

A remarkable exception is the disazo pigment derived from *o*-tolidine. The aggregation degree suggests a complex consisting of three molecules of dye and one of dispersant. The behavior is similar to that of heterocyclocetone pigments which, have a superior hvdrophobicity. It can be explained by more intensive interactions with the central di-tolyl area. Harder to explain is the behavior of the pigment *o*-toluidine→Naphtol AS. One cannot exclude the association of 3–4 molecules of pigment through dipole–dipole interactions. More plausible is that polar groups as OH, CONH, N = N, are shielded by an 'aromatic cage' consisting of rings such as phenyl, tolyl, naphtyl, which then lead to a greater possibility for association through van der Waals interactions, at least at 25°C.

TABLE 3

Dispersability and Aggregation of Some Azo Pigments

Nr	*Pigment*	*M*	λ	*log P*	K^*	$\mathcal{D}$	$\mathcal{A}$
1	Aniline→2-naphthol	248	478	2.826	0.471	1.899	0.90
2	*o*-Toluidine→2-naphthol	260	397	3.330	0.623	2.396	1.13
3	*m*-Toluidine→2-naphthol	260	504	3.330	0.421	1.619	0.76
4	*p*-Toluidine→2-naphthol	260	520	3.330	0.473	1.819	0.86
5	*p*-Anisidine→2-naphthol	276	515	2.897	0.408	1.478	0.70
6	*p*-Phenetidine→2-naphthol	290	518	3.427	0.565	1.948	0.92
7	*m*-Chloroaniline→2-naphthol	282.5	508	3.550	0.566	2.004	0.95
8	*p*-Nitroaniline→2-naphthol	293	470	2.550	0.610	2.082	0.98
9	2-Naptol←*o*-tolidine→2-naphthol	518	528	6.433	3.502	6.761	3.19
10	2-Naphthol←*o*-diansidine→2-naphthol	550	565	5.567	1.718	3.124	1.47
11	*m*-Chloroaniline→Naphthol AS	401.5	505	3.957	1.217	3.031	1.43
12	*m*-Chloroaniline→Naphtol AS-D	415.5	380	4.441	1.032	2.484	1.17
13	*m*-Chloroaniline→Naphtol AS-SR	445.5	408	4.473	1.285	2.884	1.36
14	*m*-Chloroaniline→Naphtol AS-RS	480	410	5.220	1.898	3.954	1.87
15	*m*-Chloroaniline→Naphtol AS-SW	451.5	508	5.271	1.814	4.018	1.90
16	*m*-Chloroaniline→Naphtol AS-ITR	496	490	4.787	1.952	3.935	1.86
17	*o*-Toluidine→Naphtol AS	381	396	3.737	2.609	6.848	3.23
18	*p*-Nitroaniline→Naphtol AS	414	470	2.957	1.248	3.014	1.42

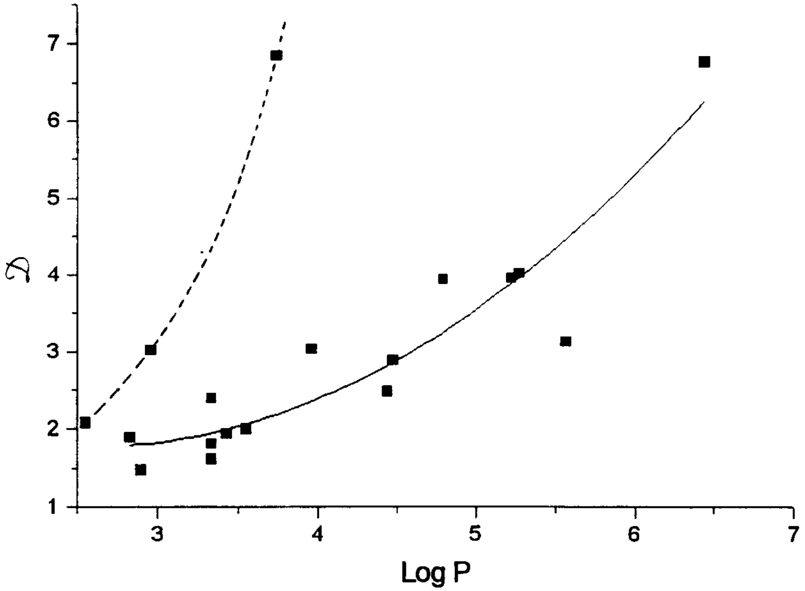

Fig. 3. Dispersability of azo pigments vs hydrophobicity.

Another exception is the case of pigments derived from *p*-nitroaniline, which as much as those of the *o*-toluidine→Naphtol AS type, exhibit a greater dispersability than the rest of the series.

An attempt of correlation of calculated log P with both dispersability and aggregation is presented in Fig. 3. Again, the dispersion of data is considerable and the model precision is poor. For the case of Dispersil WS eqns (4) and (5) resulted:

$$1/\mathcal{D} = -0.198 + 2.27/\log \mathrm{P} \quad n = 16;\ r = 0.909;\ s = 0.573;\ F = 66 \qquad (4)$$

$$1/\mathcal{A} = -0.42 + 4.8/\log \mathrm{P} \quad n = 16;\ r = 0.908;\ s = 0.271;\ F = 66 \qquad (5)$$

The pigments derived from *p*-nitroaniline and *o*-toluidine were excluded and they fit well ($r = 0.999$, dotted curve in Fig. 3) in a linear function of the form log $\mathcal{D}$-f(log P).

The amount of dispersant needed is greater than for the polycycloketone pigments, being in the limit of 0.28÷2.4 grams dispersant gram of dye^{-1}. This offers guideline data for the dispersant amount needed for the industrial conditioning of these and other similar products.

CONCLUSION

It is shown that the aggregates of dispersant with in-situ formed dye contain 1÷10 dye molecules for one of dispersant. The aggregation degree and dispersability of dyes increase with hydrophobicity and depend on the structural type of the dye.

REFERENCES

1. Bird, C. L. and Boston, W. S. (eds) *The Theory of Coloration of Textile.* The Dyers Company Publications Trust, Bradford, 1975.
2. Bohm, W., Deubach, E., Weiser, D. and Herman, M., German Patent No. 2301 638/13.01, 1973.
3. Stanley-Short, W. and Chaten, H., British Patent No. 1507 772/30.01, 1976.
4. Falkehag, S. L. and Bayley, C. W., USA Patent No. 3870 681/11.03, 1975.
5. Molls, H. H. and Torle, R., German Patent No. 2607 122/21.02, 1976.
6. Bockmann, K., German Patent No. 3847532/02.11, 1978.
7. Daescu, C. (in press).
8. Rekker, R. F., *The Hydrophobic Fragmental Constant.* Elsevier Publishing Co., Amsterdam, 1977.