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The degree of crystal aggregation in organic pigments

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Dedicated to Dr. Geoff Hallas on the occasion of his 65th birthday

Abstract

Organic pigments are normally dispersed as fine crystals, which have a marked tendency to cluster into aggregates. Pigment crystal aggregation is technologically undesirable, for it hinders the attainment of high colour strength by reducing the effective level of subdivision of the crystals. Two methods of assessing the degree of crystal aggregation are presented, both of which compare the BET surface area, determined from nitrogen adsorption isotherms, with the mean specific surface areas of the crystals. In the first method, the specific surface areas of the crystals are determined from the principal crystal dimensions. In the second method, a refinement is proposed based on the fractal nature of the pigment crystal surfaces. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Organic pigments; Crystal aggregation; Surface area; BET surface area; Fractal analysis

1. Introduction

Organic pigments are insoluble in the media to which they are applied and so have to be dispersed as finely divided crystals, typically of dimension 0.02–0.5 μm. Thus, the perceived colour of a pigmented material is determined not only by the pigment's chemical constitution but also by the size and shape of the pigment crystals. Being of such small dimension, the crystals have a marked tendency to cluster into aggregates. Such aggregation is technologically undesirable, since it hinders the attainment of high colour strength by reducing the effective level of subdivision of the pigment crystals [1]. Here, in accord with a IUPAC recommendation [2], the term "aggregation" is used to describe any form of crystal assembly.

The geometry of the crystal aggregates comprising a particular organic pigment is often strongly influenced by the geometry of the crystals themselves [3,4]. Moreover, the roughness of the individual crystal surfaces may influence aggregate geometry: pigment crystals with rougher surfaces may adhere to one another to different extents than crystals of the same chemical type with smoother surfaces [5]. Thus, any method for assessing the degree of pigment crystal aggregation should include both the geometry of the crystals and their surface roughness. With these points in mind, this paper outlines developments in assessing the degree of crystal aggregation in β-copper phthalocyanine (blue) pigments and calcium 4B toner (red) pigments.

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2. Application of specific surface area determinations

The comparison of the specific surface area of individual crystals and of the aggregates they form provides one approach to assessing the degree of pigment crystal aggregation. In this method, the mean geometric surface area, S, of the crystals of a given organic pigment is calculated from the crystal dimensions, determined from transmission electron micrographs of the pigment crystals [4] or from a combination of electron micrographs and X-ray diffraction patterns [6]. The value of S obtained is then compared with the corresponding value of S_{BET}, the specific surface area derived from the nitrogen adsorption isotherm using the Brunauer–Emmett–Teller (BET) equation [7]. It has been shown that for a number of β-copper phthalocyanine and calcium 4B toner pigments, the ratio, S_{BET}/S, is close to unity, and it is suggested that for these pigments, all of the pigment crystal surfaces are readily accessible to nitrogen during the determination of an adsorption isotherm [4,6]. For many other pigments investigated, however, the ratio, S_{BET}/S, is substantially less than unity; the surfaces of these crystals are evidently much less accessible to nitrogen. It is concluded that in these pigments there is substantial contact between the faces of adjacent crystals, giving rise to a more closely packed aggregate structure. Thus, the ratio, S_{BET}/S, can be conveniently used as an indicator of the extent of crystal aggregation: the smaller the ratio, the more extensive the aggregation.

As an example, Table 1 lists some previously published values of S_{BET}/S for β-copper phthalocyanine pigments [4]. It can be seen that values of S_{BET}/S as low as 0.54 have been reported, an indication of extensive pigment crystal aggregation. In some cases, $S_{\mathrm{BET}} > 1$; the significance of this observation is highlighted later.

Table 1
Comparison of the values of S_{BET}/S with S_{BET}/S_u for some β-copper phthalocyanine pigments with well developed crystals

Pigment sample	$10^4 V$ (μm^3)[a]	S_{BET}/S[a]	S_{BET}/S_u
A	1.05	0.80	0.61
B	1.41	0.72	0.64
C	2.93	1.07	1.02
D	3.20	0.92	0.78
E	3.48	0.98	0.85
F	4.81	1.10	0.87
G	6.34	1.05	0.95
H	6.45	0.54	0.48

[a] Data taken from Ref. [4]. V represents mean crystal volume.

3. An approach based on fractal analysis

A difficulty with the method described above arises from the roughness which the pigment crystal surfaces may possess. To take account of crystal surface roughness, it has been shown that a fractal approach may be usefully adopted [5,8]. This approach imposes a dimensional scale, D, on the pigment surface, such that $2 \leqslant D < 3$. For a surface which is perfectly smooth, $D = 2$, whilst for an irregular surface, the value of D lies between 2 and 3.

A surface must exhibit self-similarity [9,10], if it is to be properly described in terms of a fractal dimension, D: the same type of geometric features can be identified either at different magnifications or where probes of different sizes are used to examine the solid surface. One approach is to utilise the same adsorbate, often nitrogen, on a family of related pigments. The values of S_{BET} for the pigments can be analysed as a function of their crystal dimensions, d. If the pigment surfaces are fractal, then $S_{\mathrm{BET}} \propto \mathrm{d}^{D-3}$. A plot of log S_{BET} against log d is linear, with a gradient of (D-3). If the crystal dimensions are highly disperse, however, their particle distribution should be taken into account, and a more complex relation between S_{BET} and d then emerges [11].

This method is useful for pigments whose crystals are isotropic, but the crystals of most organic pigments are distinctly anisotropic. Thus, well developed β-copper phthalocyanine pigment crystals have a cuboid shape of square cross-section [4,5], and calcium 4B toner crystals are plate-like [6,8].

To account for this anisotropy, the following expression has been developed [5,8]:

$$S_{\mathrm{BET}}.V \propto A^{D/2}$$

or

$$\log_e(S_{\mathrm{BET}}.V) = (D/2)\log_e A + \text{constant} \qquad (1)$$

where A is the mean surface area of each crystal and V represents crystal volume. The values of A and V may be estimated from the mean values for the principal dimensions of the pigment crystals. A log–log plot of Eq. (1) should then yield a straight line of gradient, $D/2$.

Eq. (1) is, however, valid only for those pigments free of crystal aggregation. As Fig. 1 illustrates for a wide range of calcium 4B toners studied by McKay [6], the points clearly do not all lie on one straight line. Only those points labelled ȯ correspond to pigments which are essentially free of crystal aggregation. However, there are also two groups of pigments for which S_{BET}/S is only slightly below unity. These are the three pigments represented by points ⊗ in Fig. 1, for which $S_{\mathrm{BET}}/S = 0.96$, and the three pigments represented by points ⦶, for which $S_{\mathrm{BET}}/S = 0.93$. The straight lines through both sets of points correspond to a fractal dimension of 2. Moreover, the four points ● in Fig. 1 all correspond to pigments for which $S_{\mathrm{BET}}/S = 0.75$–$0.77$. The fractal dimension calculated for this line is 1.96, close to those determined for the less aggregated pigment samples.

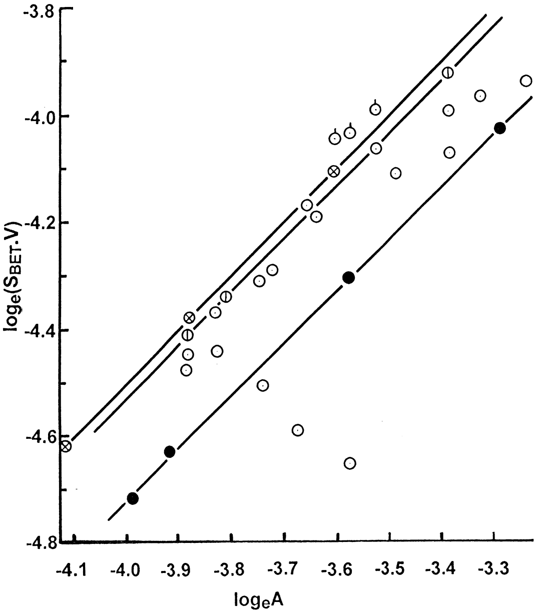

Fig. 1. A fractal plot for calcium 4B toner pigments. The data are plotted according to Eq. (1). See text for explanations of the points and lines.

It is clear then that points on the log–log plot representing extensively aggregated pigments lie below those representing less severely aggregated pigments. The position of any point in Fig. 1 for a pigment with aggregated crystals may, therefore, be compared with the position expected if the pigment crystals were completely free of aggregation. However, no reliable linear plot can be drawn for the unaggregated pigments, owing to the proximity of the points; but the line corresponding to pigments for which $S_{\mathrm{BET}} = 0.96$ may be used instead as the reference line. For each aggregated pigment, the expected position of the point on the reference line is found for the value of the abscissa in the log–log plot. The difference in the y-coordinates of the actual and expected positions of the point is $\log_e(S_{\mathrm{BET}}/S_r)$, where S_r would be the specific surface area of the crystals calculated from the reference line. S_{BET}/S_u is calculated by multiplying S_{BET}/S_r by 0.96, where S_u would be the specific surface area of the crystals in an unaggregated state. S_{BET}/S_u may be similarly calculated using, as a reference line, the line corresponding to pigments for which $S_{\mathrm{BET}}/S = 0.93$. For every pigment, the values of S_{BET}/S_u determined from the two reference lines differ by no more than 0.01.

The parameter, S_{BET}/S_u, is a measure of the extent of pigment crystal aggregation and may be compared with the equivalent value of S_{BET}/S. S_u, however, allows for surface roughness in the pigment crystals, whilst S does not. For all but two of the calcium 4B toner pigments studied by McKay, the values of S_{BET}/S_u and S_{BET}/S differ by 0.01 at most. Since from the fractal dimensions determined ($D = 2$) the pigment crystal surfaces appear to be smooth, the agreement between S_{BET}/S_u and S_{BET}/S is not surprising.

A different picture may, however, be expected from the family of β-copper phthalocyanine pigments studied [5,12]. For these pigments, it appears that $D > 2$, and so S_u would be expected

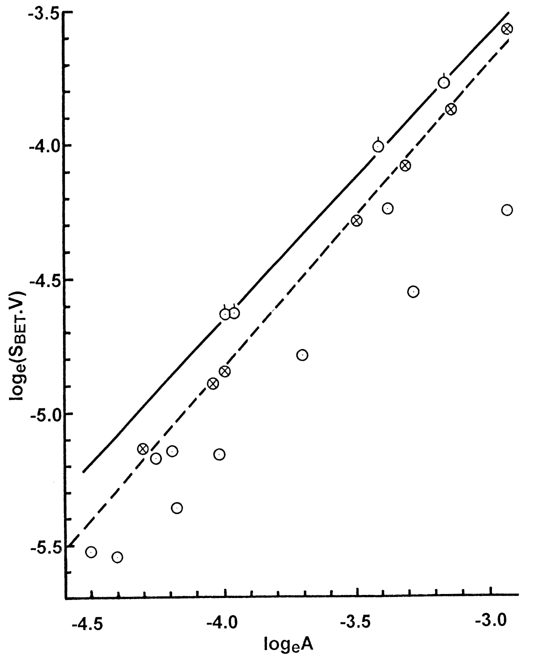

Fig. 2. A fractal plot for β-copper phthalocyanine pigments. The data are plotted according to Eq. (1). See text for explanations of the points and lines.

to be greater than S. In a previous paper [5], it was observed that, with one exception, the points in the log–log plot representing essentially unaggregated pigments appear to lie on a straight line corresponding to $D = 2.28$, as shown in Fig. 2 by the dashed line through the points ⊗. For several of these pigments, $S_{\mathrm{BET}}/S > 1$, an observation which accords with a fractal dimension greater than 2. The exceptional point lies above this line. Points ○ representing aggregated pigments lie below this line.

Since the publication of the paper, it has been discovered that points for a number of β-copper phthalocyanine pigments, not previously considered, lie above the dashed line. The points, ɸ, in Fig. 2 highlight these pigments. It appears then that the dashed line in Fig. 2 may not properly represent completely unaggregated pigments. Instead, the full line in Fig. 2 ($D = 2.14$) more closely represents unaggregated pigments, though the position of this line must still be treated with some caution, until data on further unaggregated β-copper phthalocyanine pigments are found. Nevertheless, if this line is adopted as the reference line, reasonable estimates of S_{BET}/S_u can be made for all the other pigments represented in Fig. 2. Some values of S_{BET}/S_u are compared with those of S_{BET}/S previously published [4] in Table 1. It is evident that S_{BET}/S_u is always less than S_{BET}/S. Thus, $S_u > S$, a result which is expected where the surface fractal dimension, D, is greater than 2.

References

[1] Felder B. Helv Chim Acta 1964;47:488.
[2] IUPAC manual of symbols and terminology, Appendix 2, Part 1. Colloid and surface chemistry. Pure Appl Chem 1972;31:579.
[3] Fryer JR, McKay RB, Mather RR, Sing KSW. J Chem Tech Biotech 1981;5:371.
[4] McKay RB, Mather RR. Colloids and Surfaces 1987;27:175.
[5] Mather RR. Colloids and Surfaces A 1995;98:191.
[6] McKay RB. FATIPEC Congr XVIII 1986;2/B:405.
[7] Brunauer S, Emmett PH, Teller E. J Am Chem Soc 1938;60:309.
[8] Mather RR. Dyes and Pigments 1997;34:93.
[9] Pfeifer P, Avnir D. J Chem Phys 1983;79:3558.
[10] Farin D, Avnir D. In: Avnir D, editor. The fractal approach to heterogeneous chemistry. New York: John Wiley and Sons, 1989. p. 271–293.
[11] Piscitelle L, Segars R. J Colloid Interface Sci 1992;149:226.
[12] Mather RR. Dyes and Pigments 1990;14:49.