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GRAVIMETRIC STUDIES OF THE SORPTION OF TOLUENE AND PROPANOL BY COPPER PHTHALOCYANINES

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ABSTRACT

Sorption isotherms of toluene and n-propanol were determined at 25°C on well-characterised samples of the α and β forms of copper phthalocyanines, the measurements being made with a Cahn RG electrobalance and a McBain-Bakr spring balance. A study of sorption hysteresis was undertaken with each solid–vapour system. The work demanded reliability of instrumentation for the measurement of small changes in mass over long periods of time (up to several months).

The toluene isotherm data obtained with the sample of β-copper phthalocyanine appear to be fairly straightforward to interpret: the solid–vapour interaction is relatively weak and hysteresis is confined to the capillary condensation range. On the other hand, the sample of α-copper phthalocyanine underwent considerable ageing when exposed to toluene vapour; the toluene isotherms show low-pressure hysteresis and indicate strong solid–vapour interaction.

The initial n-propanol adsorption isotherms on the β-copper phthalocyanine is Type III in character, but desorption resulted in the strong retention of alcohol molecules at very low pressure. The uptake of n-propanol by the α-copper phthalocyanine was much larger than that given by the β form and appreciable ageing occurred on exposure of the sample to n-propanol vapour.

These results reveal that the β-copper phthalocyanine sample was more stable when exposed to toluene or n-propanol than the α form (although the original surface areas were similar). Toluene adsorption appears to be restricted to the crystal surface of the β-copper phthalocyanine, whereas the sorption of toluene and n-propanol by the α form involves penetration within the pigment aggregates. The irreversible sorption of n-propanol may be partly due to slow intercalation.

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INTRODUCTION

Gravimetric methods have been extensively used in determining the mass of gas or vapour sorbed by a powdered solid. The sorption balance takes the form of either a simple helical spring, or a more sophisticated microbalance.

Recently, much interest has been focussed on the surface properties of organic pigments, in particular of copper phthalocyanines[1-3]. In the powdered form, pigments generally consist of crystalline aggregates (or agglomerates). The degree to which a pigment can be dispersed in a suitable medium depends on the structure and behaviour of the aggregates, as well as on the nature of their constituent crystals[1,4].

These properties may be investigated by means of sorption techniques. The sorption of argon and nitrogen has been applied in characterising the surface properties and aggregate structures of a variety of powdered samples of copper phthalocyanine[5]. In this case a volumetric method was used. Where, however, the sorptive exists as a vapour rather than as a gas, volumetric methods become invalidated, and gravimetric methods assume an important rôle.

Gravimetric methods have now been extended to several pigments. In this contribution, we illustrate how these methods have been applied to the sorption of toluene and n-propanol on two samples of copper phthalocyanine, and how the results highlight many differences in their properties. The results also demonstrate the need for a balance which remains reliable over a long period of time, and can accurately measure differences in mass of only a few micrograms.

EXPERIMENTAL

Of the two samples of copper phthalocyanine investigated, one contained crystals of the α-polymorph, and the other contained crystals of the β form. The preparation and purification of both samples had been undertaken in the laboratories of Ciba-Geigy (U.K.) Limited. The purification involved initially the use of Soxhlet extraction of non-pigmentary material in a variety of solvents, for several weeks. In the subsequent stages of the reduction to pigmentary form, the use of surfactants was avoided, and only AnalaR grade reagents were employed.

Volumetric nitrogen sorption isotherms were determined at 77 K, with a semi-micro apparatus similar to that designed by Harris and Sing[6]. Equilibrium pressures were measured on a mercury manometer with the aid of a cathetometer (to ± 0.002 cm). The temperature of the cryostat bath was measured with an oxygen vapour pressure thermometer.

Toluene sorption isotherms were obtained gravimetrically using a McBain-Bakr fused quartz spring balance and sensitivity $\pm 10^{-5}$ g. The spring was thermostatted at 27°C, and the pigment samples were maintained at 25°C. The extension of the spring was monitored by a cathetometer (to ± 0.002 cm). Equilibrium pressures were measured with a Bell and Howell pressure transducer gauge, with a range of 0–17 kN m^{-2} and a sensitivity of ± 7 N m^{-2} (0.05 Torr). The gauge was calibrated against a mercury manometer, using toluene vapour. Each sample was outgassed to less then 0.01 N m^{-2}, for at least 16 h at room temperature, prior to sorption measurements.

Studies of toluene vapour sorption were often complicated by aging (see below) of the pigment, when in contact with the vapour. The aging process has the effect of reducing the pigment's sorptive capacity. Although aging was slower than attainment of sorption equilibrium, it was sufficiently fast to necessitate speedy completion of each sorptive cycle. For each pigment, four isotherm cycles were recorded, the pigment being outgassed between cycles. Each cycle was completed within a day. The first cycle extended only over a reduced relative pressure range (below about 0.5), to test for reversibility at low pressures. The next cycle, over the complete attainable pressure range (up to about 0.8) followed immediately after outgassing. The sample was then treated with toluene vapour (relative pressure of 0.7 to 0.8) for 3 to 4 days, before the next desorption branch was recorded. The last cycle again covered the full attainable pressure range. Finally, the sample was outgassed for at least 24 h, before being transferred to the volumetric apparatus for sorption measurements with nitrogen.

The n-propanol isotherms were determined at 25°C on a Cahn RG electrobalance. Equilibrium pressures were measured with a Bell and Howell transducer gauge (range 0–100 kN m^{-2}) with a sensitivity of ± 13 N m^{-2} (± 0.1 Torr). The gauge was calibrated against a conventional mercury manometer with the aid of a cathetometer, and was found to be stable to within ± 26 N m^{-2} (± 0.2 Torr) for

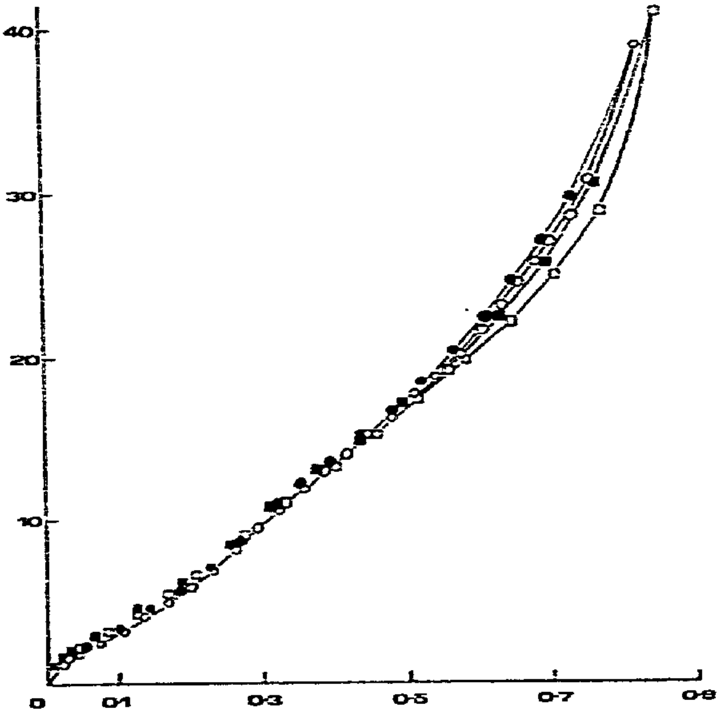

Fig. 1. Sorption of toluene by β-copper phthalocyanine, ○ ●, adsorption and desorption in Cycle 2; □ ■, adsorption and desorption in Cycle 4. Cycles 1 and 3 are not shown. Ordinate: change in mass (mg g^{-1}); Abscissa: relative pressure.

several months. For each pigment, two isotherm cycles were recorded, and the pigment sample was outgassed between the first and second cycles.

THE TOLUENE ISOTHERMS

The toluene vapour isotherm for the sample of β-copper phthalocyanine is shown in Fig. 1. For clarity of presentation, only two of the four sorption cycles have been drawn. The cycles are similar in that hysteresis is largely confined to relative pressures above 0.4, i.e., in the capillary condensation range. The cycles differ in that the amount of toluene which can be sorbed is slightly reduced from one cycle to the next. Such a progressive reduction indicates that the sample is aged by toluene vapour, although the extent of aging is small.

Figure 2 illustrates the very different sorption behaviour of toluene on the sample of α-copper phthalocyanine. The α-analogue adsorbs considerably more toluene than does the β form. The first sorption cycle is particularly interesting in that over part of it (at higher pressures) the desorption branch lies below the adsorption branch. Thus, the α-sample is very readily aged by toluene vapour. In the succeeding cycles (2 and 4), hysteresis is far more pronounced than for the β-material and is observed throughout the whole range of relative pressures applied. Successive cycles

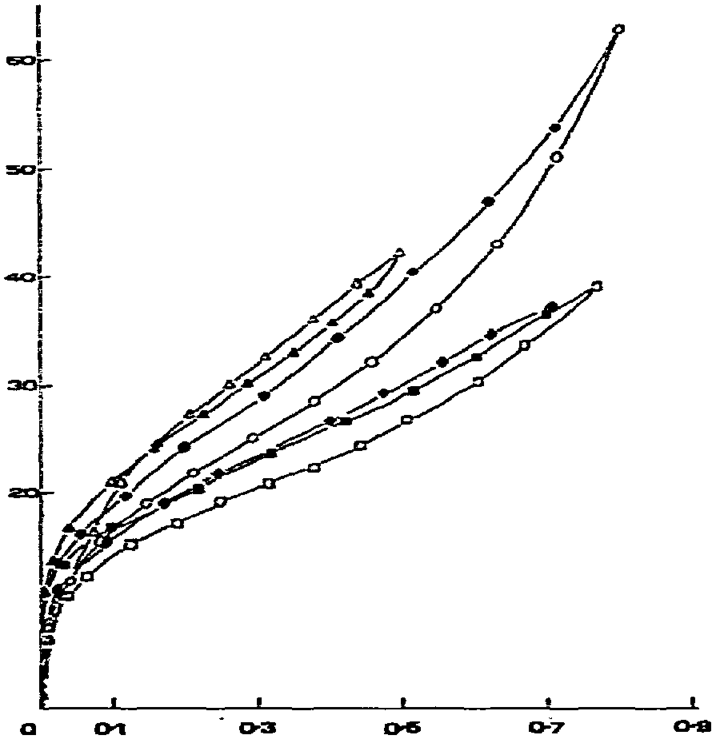

Fig. 2. Sorption of toluene by α-Copper phthalocyanine. △ ▲, Cycle 1; ○ ●, Cycle 2; ◆, Cycle 3; □ ■, Cycle 4. Filled points indicate desorption. Ordinate: change in mass (mg g^{-1}); abscissa: relative pressure.

TABLE 1

COMPARISON OF B.E.T. PARAMETERS FOR THE SORPTION OF NITROGEN, BEFORE AND AFTER AGING BY TOLUENE VAPOUR

Sample	*Unaged*		*Aged*	
	Specific surface area ($m^2 g^{-1}$)	*c*	*Specific surface area* ($m^2 g^{-1}$)	*c*
β-Copper phthalocyanine	43	32	39	36
α-Copper phthalocyanine	49	39	14	32

show a large reduction in the uptake of toluene vapour. Toluene ages the sample considerably.

Nitrogen sorption isotherms were performed on each sample, both before the start of a toluene vapour isotherm and after its completion. All the nitrogen isotherms were type II, in the classification of Brunauer et al.[7]. Table 1 lists comparisons of the B.E.T. *c*-values and nitrogen surface areas. Although the surface areas of the two unaged samples differ only a little, there is a large difference between those of the aged samples. No significant change in the *c*-values is observed: the affinity of the pigment surfaces for nitrogen is thus not appreciably altered.

THE N-PROPANOL ISOTHERMS

The isotherm for the sorption of n-propanol by the sample of β-copper phthalocyanine appears in Fig. 3. The adsorption branch of the first cycle is Type III[7] in

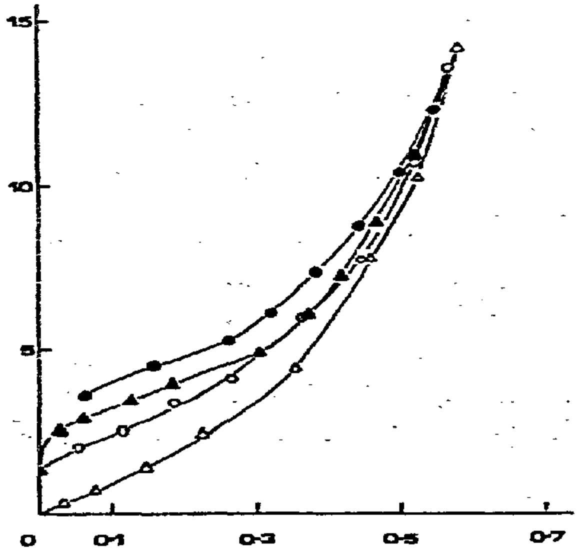

Fig. 3. Sorption of N-propanol by β-copper phthalocyanine, △ ▲, Cycle 1; ○ ●, Cycle 2. Filled points indicate desorption. Ordinate: change in mass (mg g^{-1}); abscissa: relative pressure.

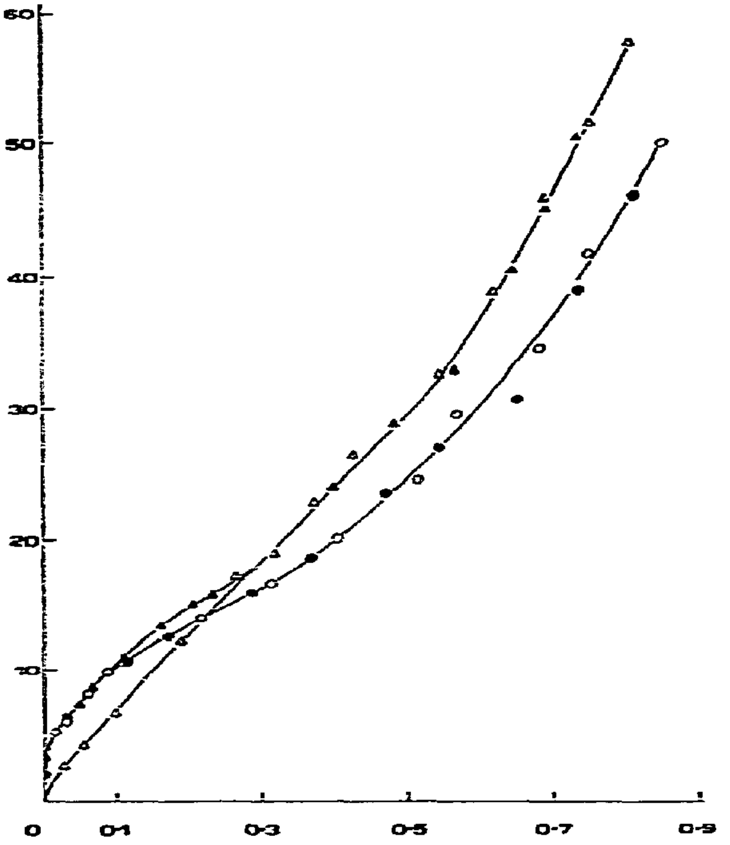

Fig. 4. Sorption of N-propanol by α-copper phthalocyanine, △ ▲, Cycle 1; ○ ●, Cycle 2. Filled points indicate desorption. Ordinate: change in mass (mg g^{-1}); abscissa: relative pressure.

character. Upon desorption, hysteresis becomes more and more pronounced as the relative pressure is lowered. Indeed, some of the alcohol molecules are so strongly retained that they remain sorbed even after outgassing of the sample. The adsorption branch of the second cycle lies above the preceding adsorption branch, but approaches it at higher pressures. Here, no aging is observed. Like the first cycle, the second cycle exhibits considerable hysteresis at lower pressures.

Figure 4 illustrates the isotherm for the sorption of n-propanol to the sample of α-copper phthalocyanine. As with toluene, the α-sample sorbs n-propanol in far greater amounts than the β-sample. The first sorption cycle seems reversible except at low pressures, and some n-propanol is retained when the sample is outgassed. The second cycle appears to be almost reversible, and is typically Type II in character. At higher pressures, it lies below the first cycle, an indication that n-propanol vapour appreciably ages the α-sample.

DISCUSSION

The sorption isotherms demonstrate the very different behaviour of the two samples of copper phthalocyanine. The α-material has a greater sorptive capacity, and is more susceptible to aging.

To understand these differences more fully, it is helpful to examine the shapes of the pigment crystals, and the structures of the crystal aggregates. Transmission electron microscopy has revealed that the β-material consists of bundles of needle-shaped crystals of length around 0.1 μm, with a length-to-breadth ratio of ca. 10. On the other hand, the α-material consists mainly of shorter plate-like crystals (0.01–0.03 μm long) arranged in more compact aggregates.

In the isotherm for the sorption of toluene to the β-material (Fig. 1) there is hysteresis at relative pressures above 0.4. From the morphology of the pigment, it appears that toluene can condense in the voids between the needle-shaped crystals. The extent of the capillary condensation (and its associated hysteresis) is small, since clusters of needles may not readily form voids of suitable dimensions for capillary condensation. The condensed toluene thus appears to age the pigment only slightly.

The affinity of the surface of the β-material for n-propanol is very low as seen from the small uptake at low relative pressures (Fig. 3). As the pressure is increased, however, the uptake becomes much greater, an indication that the sorptive now has sufficient driving force to begin to penetrate into the bundles of needle-shaped crystals. The very strong retention of alcohol molecules during desorption and outgassing may in part reflect slow intercalation into individual pigment crystals.

By contrast to toluene sorption, successive sorption cycles with n-propanol show a progressive increase in the sorptive capacity for the vapour. There is no evidence that n-propanol vapour ages the pigment.

The sorptive capacity of the α-material is considerably higher than that of the β-material. The enhanced uptake of toluene at low relative pressures shows an increased sorbate–sorbent interaction, and suggests that the aggregates may be microporous to toluene (Fig. 2). Since aging was observed at relative pressures below 0.4, it need not involve condensed toluene. The large hysteresis loops in cycles 2 and 4 do, however, suggest that there is extensive capillary condensation at higher pressures. It almost certainly occurs within the voids between the plate-like crystals of the aggregates. Moreover, since aging is accompanied by a sharp fall in nitrogen surface area, it probably arises from cementation of the crystals comprising the aggregates.

The α-sample is also aged a little by n-propanol vapour (Fig. 4). The steepness of the adsorption branch of the first cycle indicates penetration of this vapour too into the crystal aggregates. Capillary condensation, however, is absent. Thus, as was seen from the toluene isotherm, the sorbate need not be condensed to produce aging. Again, the strong retention of n-propanol molecules during outgassing is evidence for their intercalation into the pigment crystals. The apparent reversibility of the second sorption cycle suggests that the aging process has been substantially completed in the first cycle.

From this discussion, it is clear that much of the understanding of the behaviour of each pigment sample arises from measurements in the isotherm of small differences in sorptive capacity, either from cycle to cycle, or even within a cycle. In many instances, these differences are small, and are determined from experimental readings spread out over several days, or even weeks. Reliable instrumentation has therefore been essential for monitoring the differences accurately over such an extended period of time. Gravimetric equipment has provided that instrumentation.

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