

$$\text{Br}' < \text{Cl}' < \text{F}' < \text{ClO}_3' < \text{NO}_3' < \frac{1}{2} \text{SO}_4''.$$

This series is equal to that of the anionic hydration entropies. That is, ϵ_a is more anodic as the corresponding anion is more difficult to be dehydrated. C_h , the capacity at hump, shows the following series,

$$\text{Br}' > \text{Cl}' > \frac{1}{2} \text{SO}_4'' > \text{NO}_3' > \text{F}' > \text{ClO}_3'$$

This series is equal to that of the anionic deformability.

These features give important suggestions for the structure of the double layer. We are now developing its analysis, which will be presented in the next article.

8. The Transformation of Cu-phthalocyanine Crystal

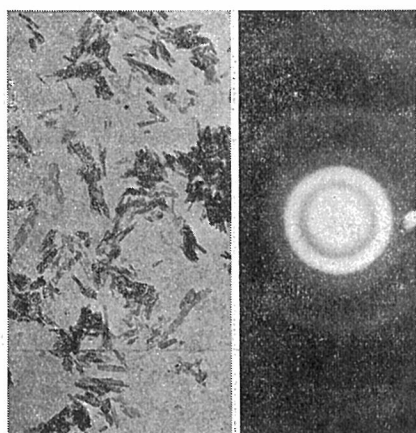
Electron Microscope and X-ray Diffraction Study

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The crystal growth of Cu-phthalocyanine suspended in some aromatic solvents was investigated. The original particles purified by dispersing the conc. H_2SO_4 solution into water are small flakes (Type I). When they are treated in some aromatic solvent such as benzene, toluene, xylene, pyridine, etc., change of shape and size take place and they grow up to some band-shaped flakes (Type II). (See this Bull., **31** (1953)53.) The x-ray diffraction patterns of both type I and II were taken to detect the change in crystal structure by a x-ray camera of Laue type, whose camera length is about 7.5 cm. The wave length of the x-ray used was 1.54 Å of $\text{CuK}\alpha$ line filtered by Ni foil. On the other hand, electron micrographs of those several specimens, whose x-ray patterns were obtained already, were taken by the electron microscope SM-C2. The photo 1(a) shows that the particles of type I are small flakes, whose size is about 0.05μ in width and 0.4μ in length. The x-ray pattern (b) shows slight diffused lines due to the smallness of the crystal size (type a). The electron micrograph of the specimen treated in toluene at 50°C and elongated to the band-shaped flaky crystals whose size is about 7μ in length and 0.5μ in width, is shown in Fig. 2 (a) and their diffraction pattern in (b), which is different from the one belonging to type a . The number of the detectable diffracted lines was much more increased compared to the former one. This shows that the crystal growth to the type II does not take place without accompanied by the crystal structure change.

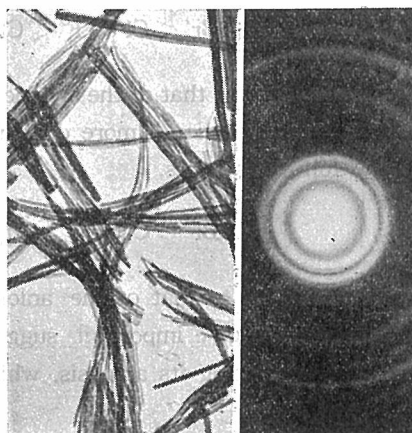
When the crystals of type I was treated by various kinds of other aromatic sol-



(a)

(b)

Fig. 1.

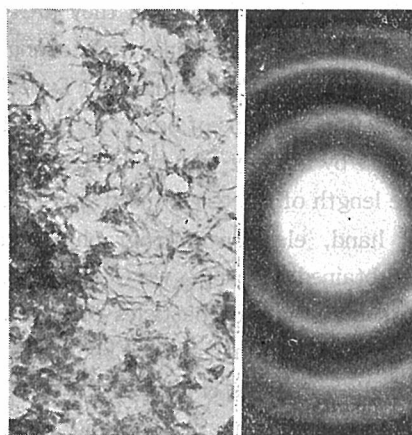


(a)

(b)

Fig. 2.

vents, the crystal growth also took place. The shape of the resulting crystals were different from one another according to the kind of the solvent used, but the x-ray diffraction patterns were similar to the one shown in Fig. 2 (b), which is called the type β . This shows that, though the crystal shapes differ one another, the crystal structure is same for these elongated specimens of type II. When the particles of type II was dissolved in conc. H_2SO_4 and dispersed in pure water at low temperature, very fine flaky particles as shown in Fig. 3 (a) were obtained. They are rather alike to the particles of type I. The x-ray diffraction pattern of the new particles are also



(a)

(b)

Fig. 3.

alike to the one belonging to type α , though some mixing extra lines which are characteristic to type β are to be detectable. Furthermore, when the last particles thus repurified were treated by aromatic solvent such as pyridine, the crystal growth again took place.

It is obvious by the facts that the treatment of the original particles of type I changes the particle shape to the one of type II, and that the crystal structure change also takes place as the x-ray diffraction pattern changes from type α to type β . The purification by dispersing the conc. H_2SO_4 solution into water reverses the above mentioned course, and this cycle can be repeated.

The spacings of lattice planes calculated from the x-ray diffraction patterns are compared in Fig. 4, where Robertson's data are also shown for comparison (Robertson,

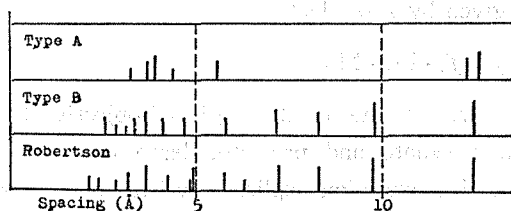


Fig. 4. Spacings of lattice planes of Cu-phthalocyanine.

J. M.: *J. Chem. Soc.*, (1937) 219). It is clear from this that the type β corresponds to the one reported by Robertson, which belongs to the space group $P_{21/a}$. It is suitable to decide that the direction of the crystal growth can be attributed to b -axis and the flaky surface observable in the electron image to $(20T)$ plane from the correspondence to Robertson's data.

9. On the Characteristic Properties of the Three-Stage Electron Microscope SM-C3 as an Electron Diffraction Camera

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The consolidated two-stage electron microscope SM-C2 was reconstructed as a three-stage electron microscope, with a projector lens newly added at the rear of the older lens system, electron diffraction chamber, and several movable apertures. This may be called the SM-C3 hereafter, and can be used as the instrument for:

1. Electron microscope having the order of final magnification continuously variable within the range from $500\times$ to $12,000\times$.
2. Dark field electron microscope with the movable objective aperture.
3. Electron micro-diffraction camera for the selected and limited area of the intermediate image of the specimen.
4. Electron shadow microscope.
5. High resolution electron diffraction camera with variable camera length, which can be also fixed if needed.