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Crystal Structure of a Crossed-Chain Potassium Soap

IT is generally assumed that hydrocarbon chains in soaps all lie parallel to each other, although experimental evidence on this point has hitherto been lacking. Soaps crystallize in a bewildering variety of crystalline forms[1], and whereas the axes of the chains may lie parallel in some forms, they do not necessarily do so in all of them.

In the case of potassium soaps, we have encountered at least three forms, provisionally designated *A*, *B*, *C* of anhydrous, and one form *D* of hydrated, neutral even-numbered potassium soaps, each giving a different characteristic *X*-ray powder pattern. The form *A* is monoclinic, and was obtained for soaps with 4–12 carbon atoms in the chain ; long spacings *d* measured in kX. obey a formula, $d = 5{\cdot}70 + 2{\cdot}165\,N$, where *N* is the number of carbon atoms in the chain. The angle of tilt between the chain axes and the (001) plane (calculated from the increment, assuming tetrahedral angle and carbon to carbon bond-length 1·54 kX. in the chain) is therefore 59·4°.

The form *B* is probably triclinic ; it was obtained for soaps with 12–18 carbon atoms per molecule. Long spacings obey the law $d = 6{\cdot}80 + 1{\cdot}95\,N$; the angle of tilt is therefore 50·7°.

The form *C* was observed only at higher temperatures, and the hydrated form *D* at lower temperatures ; they have not yet been studied in sufficient detail to warrant description. Piper[2] reports only one form each of neutral and acid potassium soaps, and the neutral soaps of longer chain-length investigated by him may be identical with our form *B*.

We were fortunate in growing a few single crystals of the monoclinic form *A* of potassium caprate ($KC_{10}H_{19}O_2$), large enough for a single-crystal X-ray examination, and prepared Fourier projections along the *a* and *b* axes. They revealed that in this form of soap the molecules are in general positions and the hydrocarbon chains cross each other at an appreciable angle.

The crystals were grown from ethanol by very slow evaporation over calcium chloride. They are extremely thin plates, the large face being {001}, with malformed edges. They are stable on exposure to the dry air, but disintegrate (probably forming the

hydrated form *D*) when exposed to air of ordinary humidity at temperatures below room temperature. Dehydration experiments showed that they are anhydrous.

Rotation, oscillation and moving film photographs were taken about the *a* and *b* axes using copper $K\alpha$ radiation. The crystal is monoclinic and the unit cell dimensions are: $a = 8{\cdot}09$ kX., $b = 5{\cdot}63$ kX., $c = 28{\cdot}81$ kX., $\beta = 108°$, d (001) $= 27{\cdot}40$ kX.; density (meas.) 1·123 gm./c.c., (calc.) 1·112 gm./c.c. (assuming four molecules per unit cell); halvings observed were: $(h0l)$ absent when h is odd, $(0k0)$ absent when k is odd; therefore, the space group is $C_{2h}^5 - P\,2_1/a$.

The intensities of the reflexions were estimated by eye and the signs of most of the structure factors determined by trial and error. In the Fourier projection along the *b* axis, the plane zigzag hydrocarbon chains project parallel to each other and edge on. Moreover, owing to a component of tilt in the plane perpendicular to the plane of projection, pairs of carbon atoms of the same chain overlap, with the exception of the terminal groups. The electron density distribution is consistent with the zigzag configuration, and, assuming the usual interatomic angles and distances, approximate x and z co-ordinates have been determined. The component of the angle of tilt projected along the *b* axis, measured from the *a*-axis, is approximately 102°. In the Fourier projection along the *a* axis the chains are seen face-on and form a criss-cross pattern, one chain making on the projection an angle of about 58°; the other, in conformity to the symmetry of the crystal, an angle of about 122°, both measured from the *b*-axis. The co-ordinates of the atoms are being refined.

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[1] Buerger, Smith, Ryer and Spike, *Proc. U.S. Nat. Acad. Sci.*, **31**, 226 (1945).
[2] Piper, *J. Chem. Soc.*, 234 (1929).

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