

This component proceeded to grow in intensity and gradually narrowed to the field homogeneity of 0.3 gauss as shown in Fig. 2 (curve B). At each temperature above the  $\lambda$ -transition the complex-line-shape could be resolved, though somewhat arbitrarily at the higher temperatures, into broad and narrow components. The broad line component, containing the majority of the intensity, is seen to give (curve A) to a close approximation the line-width temperature data for bulk methane. Thus, so far as the line-width versus temperature is concerned, the properties of bulk methane are well approximated at four monolayers under the conditions of the experiment with the exception of the narrow line component. This component is probably associated with diffusional motions initiated at the surface. As a rotational-type transformation at the  $\lambda$ -point increases the energy of a given methane molecule, it may also increase the probability for surface diffusion. This would explain the first appearance of the narrow line component at 20.9° K. A more detailed analysis of these effects is proceeding.

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<sup>2</sup> Alpert, N. L., *Phys. Rev.*, **75**, 398 (1949).

<sup>3</sup> Tomita, K., *Phys. Rev.*, **89**, 429 (1953).

<sup>4</sup> Pauling, L., *Phys. Rev.*, **36**, 430 (1930).

### Supercontraction of Wool irradiated with Ultra-violet Light or Iodinated

SUPERCONTRACTION of Corriedale wool fibres in solutions of lithium bromide (6 M–10 M), freed from bromine, has been shown to proceed in two stages, the first stage being complete at contractions of about 15 per cent and the second stage at about 40 per cent. It can be reversed up to the end of the first stage by washing out the lithium bromide with water. If supercontraction is allowed to proceed into the second stage, washing can at best only partially restore fibre-length<sup>1,2</sup>. The second stage has an activation energy deduced from the temperature coefficient of the process of about 30 kcal./mol. in the lithium bromide solution. Haly and Feughelman<sup>1</sup> concluded that the fibre, at the end of both the first and second stages, acted as an elastomer which had respectively 16 and 30 residues between 'vulcanized' sites. It was suggested that at the end of the first stage the 'vulcanizing' linkages are strong polar bonds or co-operative secondary bonds (such as exist in crystalline regions) and disulphide bonds, and that at the end of the second stage only the disulphides remain.

Wool fibres, after ultra-violet irradiation from a high-pressure mercury-in-quartz source, when heated in lithium bromide solution, supercontract much more rapidly than normal fibres, and there is no indication of two-stage behaviour. These phenomena remain when wave-lengths shorter than 2900 Å. are eliminated, but a longer time of irradiation is required. In both cases the activation energy was substantially reduced.

The disulphides in wool absorb ultra-violet radiation<sup>4</sup>. Although it was found that the amount of

cystine lost after irradiation for 2 hr. by wave-lengths above 2900 Å. was approximately 25 per cent of the total, there was no further loss of cystine during 200 hr. exposure. On the other hand, increasing the time of irradiation from 2 to 20 hr. greatly increased the rate of supercontraction in lithium bromide solution. It therefore seems unlikely that this cystine fraction plays any part in the supercontraction process. Furthermore, no change in the load-extension curves of single fibres in water could be detected due to this loss of 25 per cent of cystine. Tyrosine and tryptophan at neutral pH absorb in the ultra-violet mainly between 2500 Å. and 2900 Å. in the free state. The maximum is at about 2750 Å. Incorporation into peptides results in the loss of fine structure together with a shift of absorption to longer wave-lengths<sup>3</sup>. (The absorption spectrum of horn keratin was determined by Speakman and McMahon<sup>4</sup>.) Phenylalanine, the only other aromatic amino-acid present in wool, absorbs mainly around 2600 Å.

Further evidence was sought relating to the linkages which break to permit the second contraction stage. Corriedale fibres in which the tyrosine residues had been iodinated by the Richards and Speakman technique<sup>5</sup> were contracted in lithium bromide solution. Contraction behaviour was normal up to the end of the first stage, but the subsequent rate of contraction was extremely slow. In this respect the response of iodinated fibres was similar to that of normal wool supercontracted in solutions of lithium bromide containing bromine<sup>2</sup>. Wool fibres which had been exposed to ultra-violet radiation, however, supercontracted rapidly into the final stage in solutions of lithium bromide in which a normally effective concentration of bromine is present. As a further check, in case a reaction between lithium bromide and iodinated wool might be producing side-effects, some iodinated wool was supercontracted in calcium nitrate solution, with results similar to those obtained using solutions of lithium bromide.

This evidence suggests that tyrosine may be involved in the strong polar bonds or co-operative secondary bonds which, when broken in lithium bromide solution, allow the second supercontraction stage. The evidence of Richards and Speakman<sup>5</sup> that supercontraction of iodinated fibres in a disulphide bond-breaking reagent was approximately the same as that of normal fibres is consistent with the picture of the contraction process which is outlined above. Further experimental work is in progress, and a full report will be published later.

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