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Anisotropy of water sorbed by rhinoceros horn keratin

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With 2 figures

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In a recent nuclear magnetic resonance study (1) of water sorbed by rhinoceros horn keratin a degree of anisotropy in the water was observed. The spin-spin relaxation time (T_2) was observed to be dependent on the orientation (θ) of the fibrillar or growth direction of rhinoceros horn in the steady magnetic field. Measurements were made at different temperatures and water contents on stacks of circular discs of horn 1 cm diameter and 1 mm thick with the growth direction in the plane of the discs. The angular dependence of T_2 was attributed to an anisotropic motional narrowing of the intramolecular dipolar interaction because of preferred molecular rotations about axes parallel to the fibrillar direction. The experimental points were however widely scattered and the T_2 dependence on θ did not in all cases show very precisely the behaviour required by the interpretation. This was attributed to misalignment of the fibrillar components of the rhinoceros horn both within and between discs.

Measurements have now been made on a solid cylinder of rhinoceros horn, cut so that the growth direction is in the plane of the cylinder. The results obtained show much less scatter than those obtained for the disc stacks and also reflect very closely a $[3\cos^2\theta - 1]^{-1}$ modulation in the dipolar interaction, in that there is a maximum near 55° and minima at 0° and 90°. This confirms the previous interpretation.

The results are plotted in fig. 1. The specimen contained 0.3 g of water per gram of dry horn and the angular dependence of T_2 at three temperatures, 14, 28 and 56 °C, is plotted. The T_2 anisotropy is seen to decrease with increase of temperature and to disappear at 56 °C. This anisotropy in T_2 probably decreases with temperature for two reasons (a) areal decrease in the motional anisotropy of the water molecules and (b) the onset of an exchange between the water protons and less mobile protons, which are probably labile protons of the keratin. The rate of such an exchange increases with temperature and has the effect of decreasing the measured T_2 value (2). The temperature dependence of this effect is therefore opposed to the normal temperature dependence of the dipolar spin-spin relaxation mechanism. That this exchange mechanism is effective for water sorbed by keratin is apparent from a plot of measured T_2 against temperature for water sorbed by wool keratin, fig. 2.

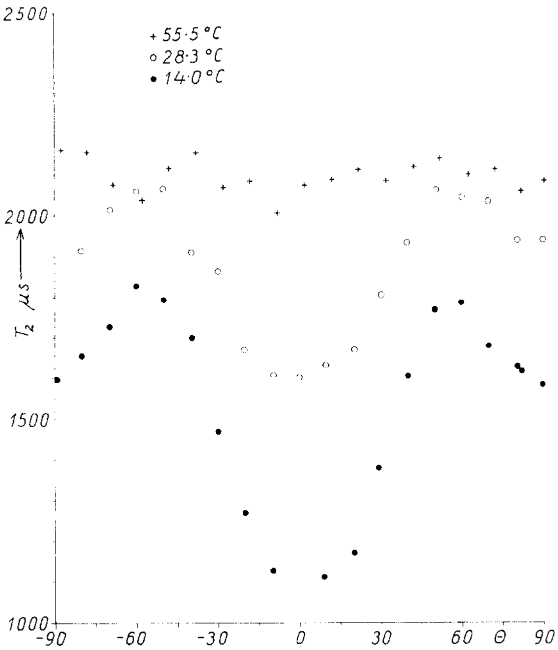

Fig. 1. Plots of T_2 against orientation in the applied magnetic field, for water sorbed by rhinoceros horn keratin at three temperatures

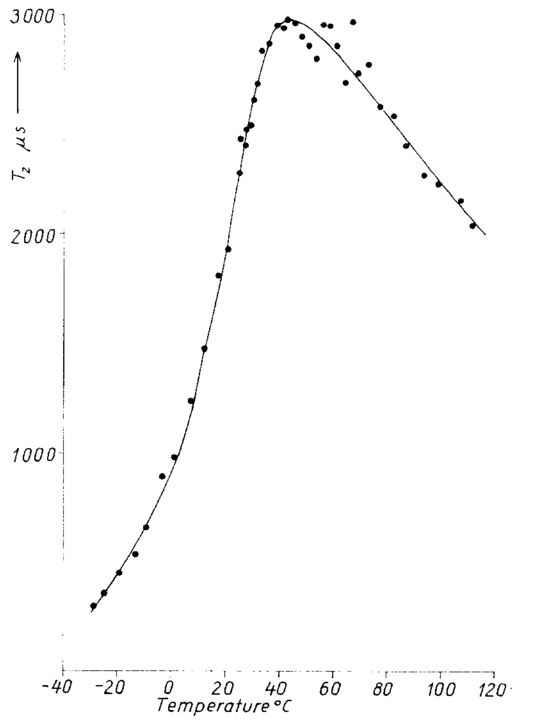

Fig. 2. Temperature dependence of measured T_2 for water sorbed by wool keratin. Water content 0.27 gm per gm of dry keratin

T_2 increases with temperature until about 45 °C and then passes through a maximum as the temperature is raised further. It is therefore likely that at higher temperatures when the observed anisotropy in T_2 for water sorbed by rhinoceros horn first disappears some motional anisotropy still exists but is not apparent from the measured T_2 values because of their dominance by the exchange effect.

Acknowledgement

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