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SOLID-LIKE WATER IN CETYL ALCOHOL

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Addition of a small amount of water to cetyl alcohol caused a marked increase of electrical conductivity in the α-state. Deuteron magnetic resonance spectra for the hydrated specimens indicate that the water molecules are contained in a solid-like state and enhance the protonic conduction presumably by the Grotthus mechanism.

Cetyl alcohol premelts and assumes in a temperature range below melting a transparent hexagonal state in which rotational movement of the molecule is partially released about its long chain axis. Cetyl alcohol in this α-state (α-phase) exhibits protonic conduction due to the Grotthus mechanism.[1)] Addition of a small amount of water is known to lower the premelting temperature and to raise the melting temperature. However, the effect of this added water molecules on the protonic conduction has remained to be studied. We made electrical conductivity measurements using polycrystalline cetyl alcohol containing various amounts of water and found that the conductivity increased 7 fold on addition of 3 % water.

Anhydrous specimen was prepared in melt by evacuating the commercially available cetyl alcohol (mp 49^{o}C) in 10^{-3}mmHg for 30 hrs. A varied amount of water was added to this specimen in its melt state and the specimen was cooled down to the α-phase temperature range at an approximate rate of 0.2^{o}C per min. The D.C. conductivity was measured in a pyrex glass tube using Pd-electrodes. Since the specimen showed the ohmic response, readings were taken 2 min after applying 3 volts. Fig.1 shows the specific conductivity as affected by the presence of water up to the solubility limit. For the sake of comparison, similar data for melt and β-solid specimens are drawn in the figure. The fact that the marked increase in conductivity is observed only with the specimen in the α-phase indicates the possibility that the water molecules take part in the protonic conduction by the Grotthus mechanism.

In this connection, high resolution NMR spectra gave no water signal with a hydrous specimen in the α-phase, while it gave broad signals with those containing the same amount of water in melt and β phases. This suggests that the water in the α-phase is in a more solid-like state than in the other phases. Deuteron magnetic resonance (DMR) spectra using deuterated cetyl alcohol confirmed this suggestion.

Deuterated cetyl alcohol was prepared by repeated exchange with D_2O. Fig.2 shows the curves of DMR spectra for the specimens in powder form obtained by using a Varian VF-16 wide line spectrometer at the deuteron resonance frequency of 8 MHz (approximately 12.2 kG). The anhydrous specimen shows a quardrupole splitting of 21 G. The addition of D_2O yielded narrower splitting and larger signal intensity, the splitting

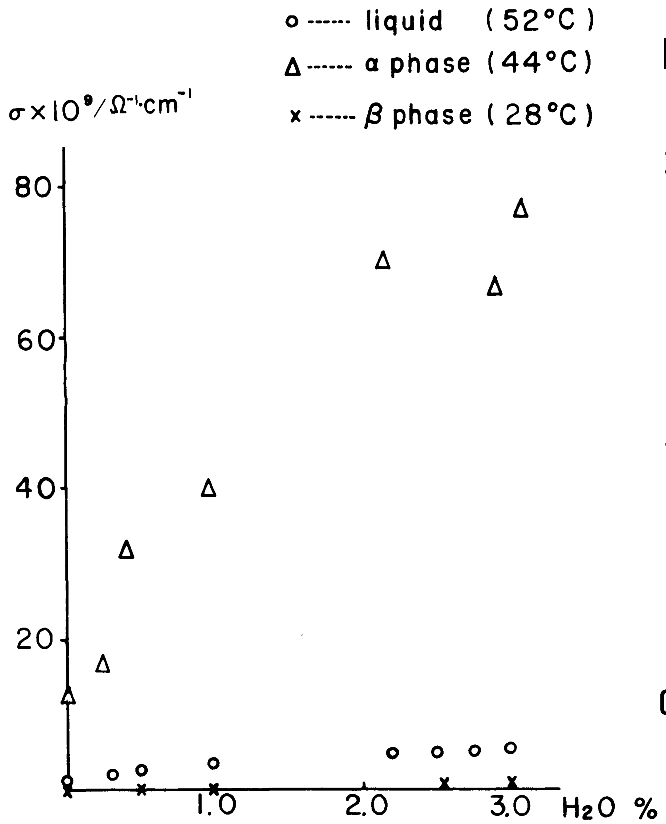

Fig. 1. D.C. conductivity of cetyl alcohol-water systems.

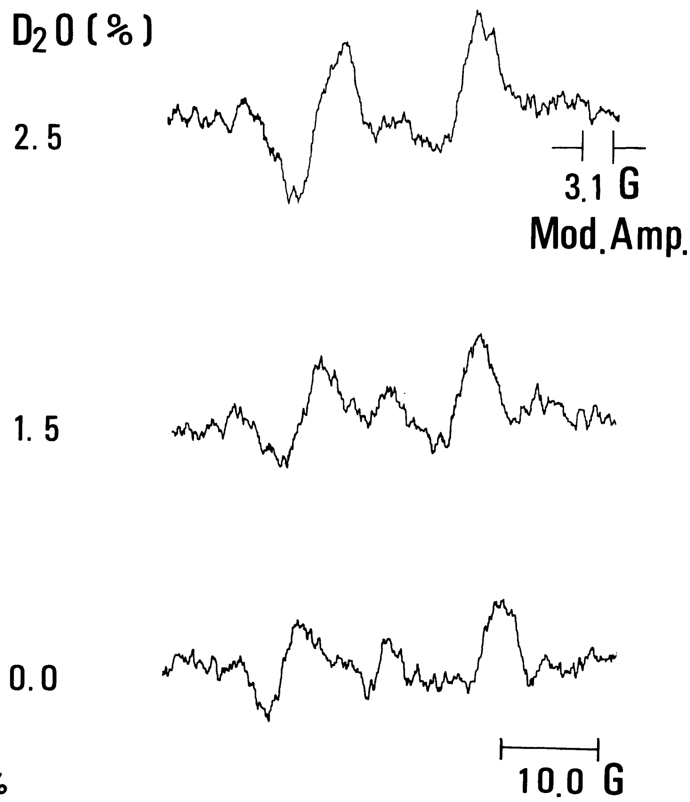

Fig. 2. DMR spectra of deuterated cetyl alcohol- deuterium oxide systems.

being 15 G for the specimen containing 2.5% water. These spectra suggest that OH groups in cetyl alcohol and hydration water are making a similar type of anisotropic molecular motion, presumably a flip-flop motion around the direction of chain molecules.[2)] This is made possible when the water molecules, being captured in a plane of the polar groups of the oriented alcohol molecules, make hydrogen bridges between two adjacent alcohol molecules. The addition of water seems to make the flip-flop motion in the hydrogen-bridged networks more accessible to jumping protons and thus results in an increased protonic conduction.

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