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CELLULOSE–AMINE OXIDE SYSTEMS

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A number of patents and scientific reports have focused recently on new organic solvents for cellulose. Among all the systems investigated, tertiary amine oxides stand out as very powerful cellulose solvents with great potential for industrial development and research (Graenacher & Sallman, 1939; Johnson, 1966; Franks & Verga, 1979).

N-Methyl morpholine *N*-oxide (MMNO) appears to be the tertiary amine oxide most commonly used to dissolve cellulose. Several aspects of the interaction of this solvent with cellulose will be considered including:

(a) its molecular interaction with OH rich substances such as cellulose;
(b) its penetration inside the cellulose crystalline lattice;
(c) its phase diagram with water and cellulose;
(d) the occurrence of a concentrated liquid crystalline cellulose solution.

The molecular interaction of MMNO with OH rich substances such as water and primary or secondary alcohols was studied by conventional crystallographic methods using single crystals of model compounds. MMNO forms a series of stoichiometric hydrates. Its phase diagram with water has been established and is shown in Fig. 1.

The active part of MMNO is its N—O group in which the oxygen readily forms hydrogen bonds with one or two hydroxyl groups (Maia *et al.*, 1981; Chanzy *et al.*, 1982). Thus cellulose can be solvated by MMNO containing little or no water. When too much water is present, however, MMNO prefers the water hydroxyl group and cellulose is precipitated out of solution.

When native cellulose fibres such as those of wood pulp or ramie are added to MMNO water mixtures of various compositions the nature of the interaction is determined by the water level. At low water contents and high temperatures, rapid dissolution of the fibre occurs without any preswelling of the fibres. With water levels of 17–20% (weight of water/weight of solvent) and temperatures of 60–70°C, the

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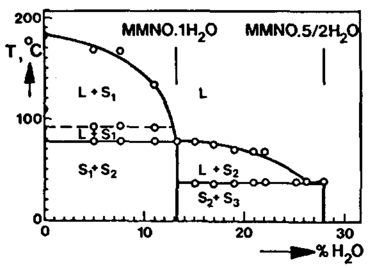

Fig. 1. Melting point/composition diagram of the $MMNO/H_2O$ system.

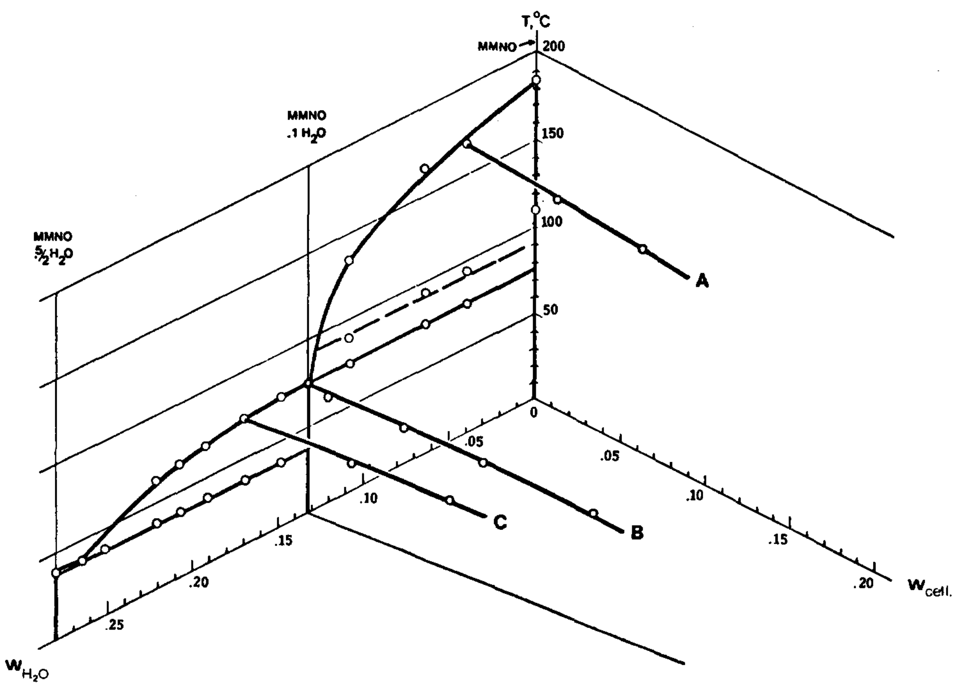

Fig. 2. MMNO-rich part of the melting point/composition diagram of the quasiternary system, $MMNO/H_2O$/cellulose.

fibres swell extensively but do not dissolve. With larger amounts of water, no interaction is detected at any temperature. This behaviour was followed on both macro and microscales using optical and electron microscopy and a suggested mode of interaction was presented.

Upon cooling dilute cellulose solutions ($<10\%$ w/w cellulose) crystallise. A three component phase diagram of cellulose, MMNO and water was established using differential scanning calorimetry. This phase diagram is presented in Fig. 2. In conjunction with the phase diagram the morphology of the crystallised solutions was also determined. Two types of morphology were obtained: cellular or spherulitic, depending on the solvent phase present (Chanzy *et al.*, 1979).

The concentrated solutions of cellulose in MMNO have a mesophase character and are birefringent when viewed under a polarising microscope. The birefringence depends on several interconnected parameters such as the DP of the cellulose, its concentration, temperature and water content. These liquid crystalline cellulose solutions are potentially interesting as they allow oriented cellulose fibres and films to be formed upon spinning or casting (Chanzy *et al.*, 1980). Their behaviour and some of their characteristics were illustrated.

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