

Phase diagram of a cellulose solvent: *N*-methylmorpholine–*N*-oxide–water mixtures

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Abstract

The phase diagram of the *N*-methylmorpholine–*N*-oxide–H₂O mixtures from 0 to 100% has been determined. Three crystalline hydrates have been identified, the already known monohydrate, a dihydrate and a hydrate composed of 8 water molecules per NMMO. The melting temperature of the 8H₂O–NMMO hydrate is –47 °C with a melting enthalpy of about 80 J/g. The region between 25 and 55% of water does not show any crystallisation, but a glass transition around –60 to –100 °C.

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1. Introduction

N-Methylmorpholine–*N*-oxide–water mixtures are direct solvents for cellulose providing that the amount of water in the mixture is not too high, about less than one molecule per NMMO molecule. Because cellulose either dissolves (under the conditions given above) or swells when the water content increases, it seems necessary to know the full NMMO–water phase diagram. It is also important since in the process of manufacturing cellulose objects from cellulose–NMMO solutions (called the Lyocell process), cellulose is first dissolved in a high NMMO-concentrated mixture, regenerated and washed in pure water. During the process, the water content goes to a bit less than one water molecule per NMMO to pure water. The necessity of knowing the phase diagram was clear from the very beginning of the studies of the NMMO–water–cellulose mixtures, and at least five papers dated from 1982 to 2001 give either structural data (thermal [1], crystallographic [2, 3]) or the phase diagram [4–6]). All the reported phase diagrams are in the range pure NMMO to 0.7NMMO–0.3water. There is no reported work for higher water content. In addition, there are a lot of discrepancies between the results of different published phase diagrams.

Fig. 1 shows the structure of the NMMO molecule. Fig. 2

shows the three published phase diagrams, re-plotted from Refs. [4–6] to have similar units for the scale of composition. As can be seen readily, there are strong disagreements on the general shape, on the number of transitions and the stable crystalline hydrates. Two stable crystals are found by all authors, the anhydrous form and the monohydrate form, 1H₂O–NMMO, or 13.3 wt% H₂O–86.7 wt% NMMO. The melting temperature of the anhydrous NMMO was found to be 184 °C [4], 184.2 °C [1], not reported in Ref. [5], and given without reference to the measurement method at 172 °C [6]. The melting temperature of the monohydrate NMMO–H₂O is given at 72 °C [5], 75 °C [4], 75.6 °C [1] and 78 °C [6]. These discrepancies can be easily ascribed to differences in the thermal instrument (all were DSC) calibration and to minor differences in the water content that has a strong effect on the DSC peak position. In addition, not all authors explain what they consider as ‘a melting temperature’ when they analyse a DSC peak. The thermal behaviour between pure NMMO and the hydrates with $n < 1$, n being the number of water molecules per NMMO molecule, is more subject to controversies. The thermal analysis gives two peaks for the anhydrous NMMO, at ~110 and 184 °C, and three for hydrates with $n < 1$, at 75, 110 and 184 °C. The peaks at 75 and 184 °C can be readily ascribed to the monohydrate and the anhydrous forms. The peak at 110 °C was ascribed either to an unknown stable hydrate in Ref. [1], to a solid-solid

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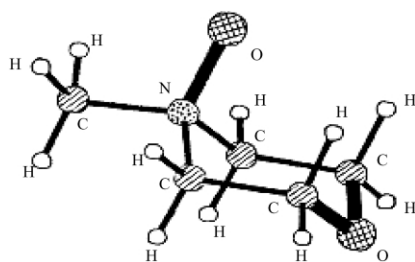


Fig. 1. Schematic representation of the *N*-methylmorpholine-*N*-oxide molecule.

transition of the anhydrous NMMO in Ref. [4], and recently to an anhydrous-monohydrate transition in Ref. [6]. The fact that the anhydrous form shows this 110 °C transition rules out the presence of a stable hydrate (like 0.5H₂O–NMMO) [1] as well as the anhydrous-monohydrate transition [6]. X-ray scattering performed upon heating, shows that it is indeed a solid-solid transition of the anhydrous NMMO [4]. The crystallographic structures of anhydrous NMMO and NMMO monohydrate are given in Refs. [2,5].

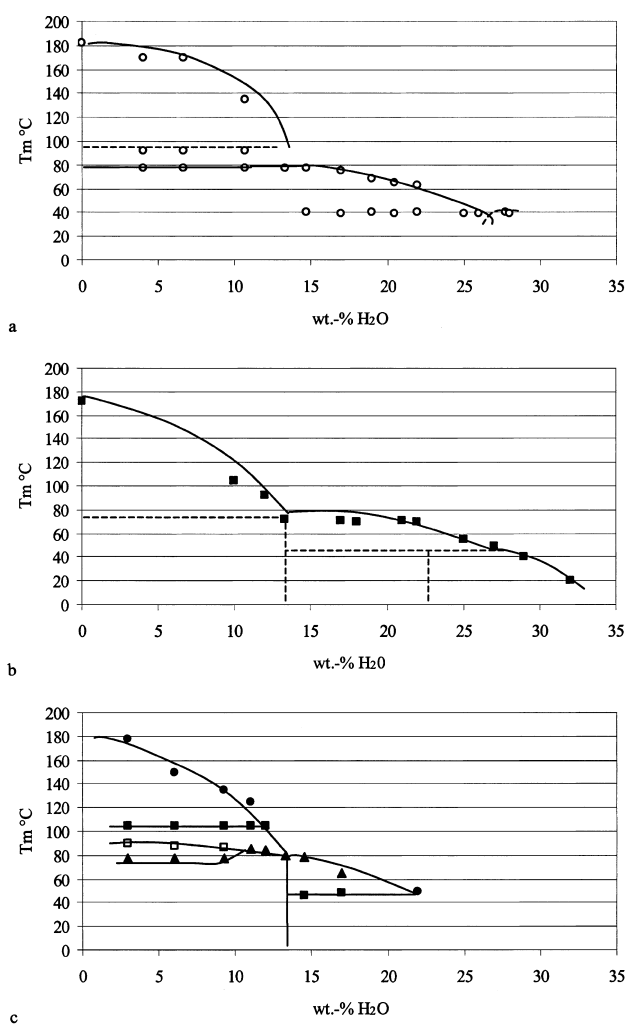


Fig. 2. Plots of three published NMMO–water phase diagrams: (a) Chanzy et al., 1982 [1]; (b) Platonov et al., 1983 [5] and (c) Kim et al., 2001 [6].

At higher water content, the situation is less clear. There is obviously a stable hydrate, with 2 [5] or 2.5 [1,3,4] water molecules per NMMO molecule, melting at 40 °C. X-ray experiments and computer calculations [3] suggested it is a 2.5H₂O–NMMO hydrate. The plotting of the phase diagram from $n = 1$ to $n = 2.5$ is very different in the three published works, as shown in Fig. 2. There is nothing known for $n \geq 3$.

The aim of this paper is to revisit the $n = 1$ to $n = 3$ phase diagram and to extend it up to pure water.

2. Experimental part

Most of NMMO–water mixtures were kindly provided by the Austrian company Lenzing AG. They were prepared by the dilution of the anhydrous NMMO. The concentration of NMMO was determined by titration. The titration method consists in addition to NMMO–water solution of the quantity of H₂SO₄ of known concentration needed to complete the reaction. The end of reaction is indicated by reaching a defined pH. The NMMO concentration is calculated from these data.

Some solutions were prepared in CEMEF. NMMO with 3 wt% of water was provided by Aldrich. NMMO–water mixtures were prepared by dilution and the water concentration was calculated by refractometry. The graph of the evolution of the refractive index of NMMO–water mixtures as a function of the NMMO concentration is shown in Fig. 3.

Scanning calorimetry measurements were performed both in CEMEF on the Perkin–Elmer DSC 7 device and in Laboratoire de Cristalochimie du Solide, Université Pierre et Marie Curie, Paris on the DSC Setaram model 92. NMMO–water solutions samples were sealed in stainless steel capsules. Experiments were performed at various cooling rates (0.5, 1 and 10 °C/min) and heating rates (3, 5 and 10 °C/min). The melting points were taken from the positions of the peak maxima. The value of the melting point obtained in this way corresponds to the temperature of disappearance of the trace of crystalline phase over a wide range of concentrations.

Optical microscopy observations at low temperatures

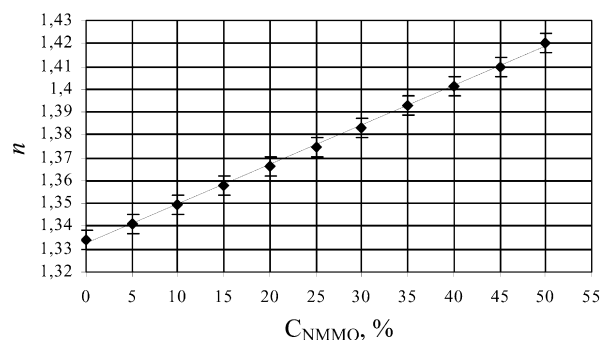


Fig. 3. Evolution of the refractive index of NMMO–water mixtures as a function of NMMO concentration.

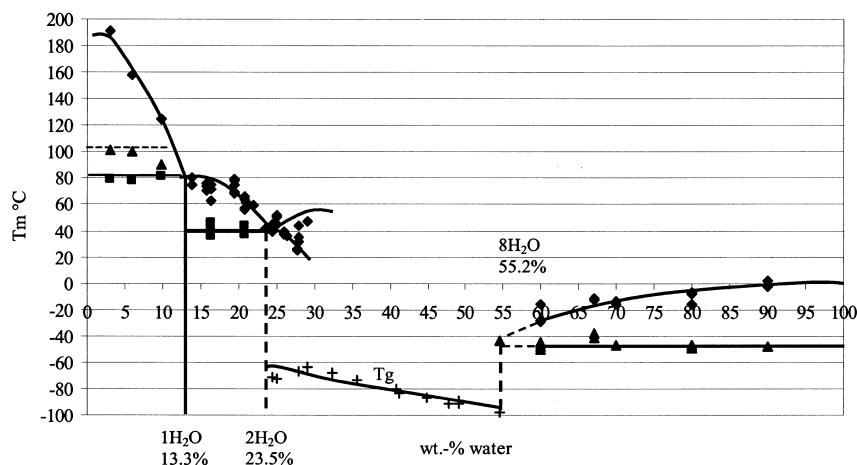


Fig. 4. Complete NMMO–water phase diagram.

were performed using a Linkam THMS 600 hot stage equipped with liquid nitrogen cooling system and a Leitz Metallux 3 optical microscope.

3. Results and discussions

The full phase diagram of NMMO–water mixtures is shown in Fig. 4. It is built from DSC experiments of many NMMO–water compositions with several calorimeters in two different locations. We will describe it part by part, starting from pure NMMO. In the following, the NMMO–water mixtures will be noted $n\text{H}_2\text{O}$ –NMMO, n being number of water molecules per NMMO molecule.

3.1. Compositions with $0 < n \leq 1$ (anhydrous to monohydrate)

The phase diagram is the one that has been already published. We show explicitly here the two crystallographic forms of the anhydrous part. This departs from the recent phase diagram of Ref. [6] that gives three co-existing

crystals at low temperatures, the anhydrous and two forms of monohydrates. We found no evidence of such a mixture, since the peak at 110 °C can be absolutely ascribed to a solid-solid transition of the anhydrous NMMO.

3.2. Compositions with $1 < n \leq 2.5$ (monohydrate to 2.5 hydrate)

The phase diagram in the $1 < n \leq 2.5$ region shows clearly the existence of a eutectic or a stable crystalline hydrate, a fact already recognised. The melting temperature of this compound is 40 °C. As shown in Fig. 4, the region above $n = 2$ is only the beginning of a two-phase composition with what looks like a liquidus and a solidus, not related to the $1 < n < 2$ compositions. This rules out the fact that the crystalline entity melting at 40 °C is a 2.5 hydrate, as claimed in Ref. [3]. A closer look at this reference shows that the X-ray scattering diagram used to define the type of crystalline hydrate is compatible with either a dihydrate or a 2.5 hydrate. The authors choose the second hypothesis on the ground of a delicate structure refinement that shows that the 2.5 case was better fitting the

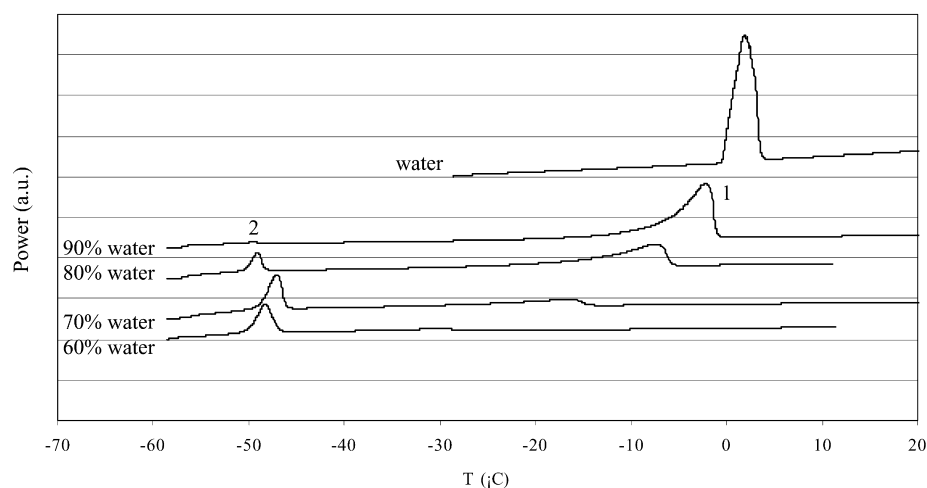


Fig. 5. DSC plots of the melting curves of NMMO–water mixtures with high water content.

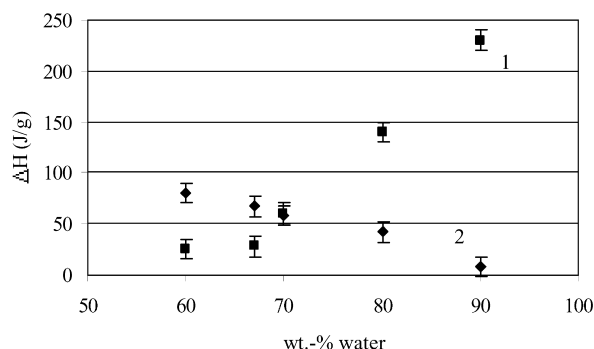


Fig. 6. Evolution of the enthalpy of melting as a function of water content of two peaks. Numbers 1 and 2 refer to Fig. 5.

X-ray data. Fig. 3 shows that the shape of the phase diagram above $n = 2$ is not compatible with the existence of a 2.5 crystalline hydrate melting at 40 °C. Owing to the large number of independent experiments that were made, we believe that there exists a crystalline dihydrate melting at 40 °C, and thus there is a two phase-region above $n = 2$, of unknown composition since the phase diagram is incomplete above $n \sim 2.5$, in terms of crystalline entities.

3.3. Compositions with $2.5 < n < 8$

In this region, only very weak DSC events are recorded in the -60 to -100 °C temperatures range, with the variation of specific heat ΔC_p as low as 1 J/(g C). We think

that these events can be related to a glass transition. A crystallisation should obviously occur, looking at the shape of the phase diagram between $n = 2$ and $n = 2.5$. But whatever was the thermal path, no crystallisation was recorded.

3.4. Composition with $n \geq 8$ (from $8H_2O$ -NMMO to pure water)

Fig. 5 shows the DSC traces of several compositions. There are clearly two peaks. Fig. 6 shows the evolution of enthalpy of melting of two peaks labelled 1 and 2 in Fig. 5. The sharp one at low temperature has a melting temperature slightly varying from -48 °C when the mixture is close to pure water to -45 °C when the mixture is close to $8H_2O$ -NMMO. The wide peak has a maximum temperature from 0 °C (pure water) down to -30 °C when it nearly vanishes. The fact that there is no visible crystallisation at composition with slightly less water than $8H_2O$ -NMMO shows that the sharp peak corresponds to the melting of $8H_2O$ -NMMO, with a melting temperature of -45 ± 3 °C and a melting enthalpy of 80 ± 10 J/g. From the DSC trace, one can plot the phase diagram in this composition region. The $8H_2O$ -NMMO is a new stable crystalline hydrate. Up to now were only known the monohydrate and the (2.5 or 2) hydrate. Fig. 7 shows the morphology of crystallising entities for NMMO–water solutions at various concentrations and temperatures. When observed with optical

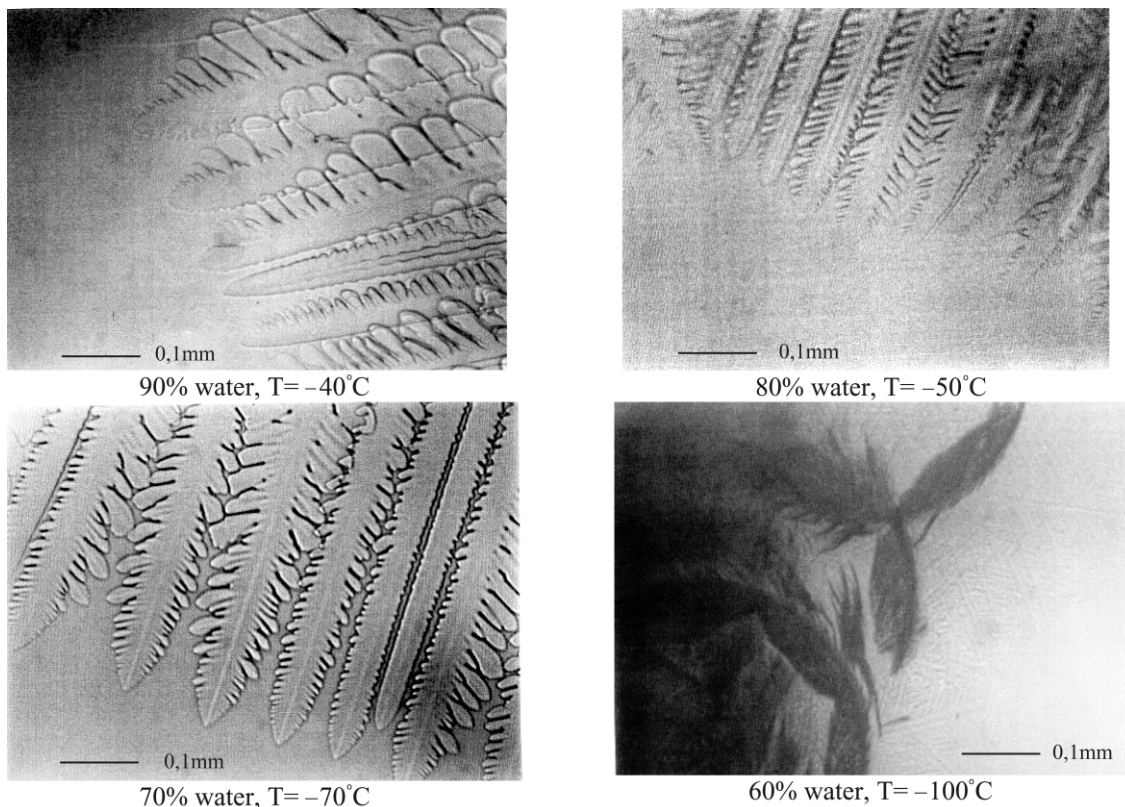


Fig. 7. Optical micrographs of the morphology of crystallising NMMO–water mixtures with high water content.

microscope in reflected light, these solutions show parallel (90, 80 and 70% of water) or fan-shaped (60% of water) dendritic lamellae. These dendrites are a very common phenomenon that is occurring with many small molar mass materials like metals or organic compounds. Water alone is known to present such perturbed crystallisation morphology. Dendritic structures have several origins like growth velocity dependency on the crystalline orientation or like thermal fluctuations. The parallel arrangement that can be seen in Fig. 7 could be due to a spinodal demixing phase change.

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