DUBBLE	Experiment title: The complex low temperature behaviour of PVME/water	**Experiment number**: **26-02-337**
Beamline: BM-26B 'Dubble'	**Date(s) of experiment**: From: 03-02-2007 To: 06-02-2007	**Date of report**: 24- 10 -2007
Shifts: 19	**Local contact(s)**: Dr. Kristina KVASHNINA	
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Report: (max. 2 pages)

In recent years we made several nontrivial theoretical predictions concerning the phase behaviour of aqueous polymer solutions with the Lattice Wertheim Theory developed in our laboratories. Most of these predictions have already been experimentally verified, except one particular prediction for which we require time resolved simultaneous SAXS/WAXS measurements.

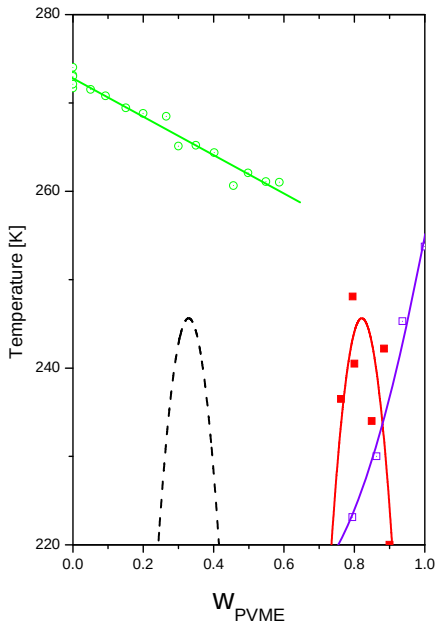

Figure 1. Low temperature phase diagram of PVME/water. Melting line of water as a function of composition (-○-); experimental high composition adjacent UCST(, -■-).; predicted low composition adjacent UCST(- - - -); Tg of PVME/water mixtures (-□-).

The relevant low temperature phase behaviour of PVME/water is shown in Figure 1. Two adjacent narrow

UCST miscibility gaps are predicted. The UCST miscibility gap at high concentrations was verified experimentally (see figure, -■-). The low concentration UCST gap is difficult to access directly as the crystallization of water interferes below the equilibrium melting line of water (figure, - -○- -) and hampers the direct observation of this UCST miscibility gap. In this temperature and composition region large super cooling can be realized and from modulated DSC experiments in the composition range $0.25 < w_{PVME} < 0.35$ for large super cooling where the crystallization of water does not yet seem to take place a thermal process is detected in the modulated DSC signals that we assign to the occurrence of L-L demixing behaviour.

In the temperature and composition region where the DSC results are obtained, we performed now simultaneous SAXS/WAXS scattering experiments at DUBBLE to prove that in the time, composition and temperature window where the DSC signals are observed no crystallization is occurring. ***Simultaneous time resolved SAX/WAXS measurements were performed for*** 5 compositions($w_{PVME} = 0.20, 0.25, 0.30, 0.35, 0.40$) and 7 modulated temperatures ($T = -10, -15, -20, -25, -30, -35, -40^0C$). At each temperature the X-ray scattering was monitored for at least 3 hours when no crystallization occurred or until crystallization occurred at the higher super coolings.
The X-ray experiments show that indeed no crystallization is observed in the time-temperature composition window where the DSC experiments show the L-L related signals. In this way we have been able to prove that these signals are NOT related to crystallization and can very well be assigned to L-L demixing.

In addition, preliminary experiments were performed in a new system studied in Leuven, i.e. N-(isopropyl)propionamide (NIPPA) /water where in the DSC results peculiar behaviour was observed. These could be attributed to a solid/solid transition. Time resolved WAXS data were collected for 5 compositions ($w_{NIPPA} = 0.10, 0.30, 0.50, 0.70, 0.90$) in the temperature range of ($T = +50.... - 30^0C$) at a cooling rate also achieved in DSC experiments, i.e. 10 degrees per minute .
The solid/solid transition has now been verified by the WAXS experiments but at the same time for intermediate compositions in the system no crystallization (WAXS signal) was observed whereas in the DSC results thermal transitions pointing to a first order transition could be observed. These data require further analysis and most likely the performance of further SAXS/WAXS experiments in the future.