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Comment on "Phase diagram of a solution undergoing inverse melting"

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The observation of a first order phase transition between two fluid phases, reported by R. Angelini *et al.* [Phys. Rev. E **78**, 020502(R) (2008)], is not supported by the measurements and is shown to be caused by the loss of solubility of alpha-cyclodextrin in the water–4-methylpyridine solvent.

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We first summarize observations made on this system by us and other groups [1–5]. As observed for some methylated β-cyclodextrins in water [6–9], the solubility of α-cyclodextrin (αCD) in 4–methylpyridine (4MP) decreases with increasing temperature, and this decrease depends on the addition of water. In solutions containing about 2% (in weight) of water the loss of solubility becomes very steep at around 70 °C. For initial concentrations of greater than about 200 mg/ml αCD, heating leads to the formation of a milky-white solid. The solid is a mixture of crystals and residual solution. The crystals contain eight to ten 4MP molecules per αCD and undergo a series of phase transitions upon further heating. Above 75 °C the solubility of αCD drops to 10–20 mg/ml [3]. Upon cooling to ambient temperature, the crystals dissolve, the initial solution is fully recovered after some time, and the process can be repeated indefinitely. All transformations as a function of temperature show considerable hysteresis, and the onset of crystallization depends significantly on the heating rate as shown in detailed calorimetric measurements on a 100 mg/ml αCD/4MP sample, where this onset increases by 10 K in increasing the heating rate from 12 to 60 K/h [2].

The observations that crystals are formed upon heating in solutions with molar ratios of 1:6:100 $\alpha\mathrm{CD}:\mathrm{H2O}:4\mathrm{MP}$ (corresponding to 100 mg/ml αCD) [1–3,5] are in clear contradiction with the claim of Angelini *et al.* [10] that "at lower concentrations, below and close to $c=150$ mg/ml, not only the intermediate solid-solid transition is no longer visible, but the whole solid phase disappears and the LTL-HTC and HTC-HTF transition lines merge into each other." (LTL: low-temperature liquid, HTC: high-temperature crystal, and HTF: high-temperature fluid).

We propose that the peak observed in differential scanning calorimetry (DSC) measurements corresponds to the formation of crystals, which went un-noticed in visual inspection. The shift of this peak to higher temperatures with decreasing αCD concentration is easily explained by the relatively high scan rate of 600 K/h which leads to a retardation as demonstrated in Ref. [2]. The analysis of all other measurements, made on such inhomogeneous fluids, remains therefore uncertain: clearly x-ray diffraction from solutions, deprived of a significant fraction of the αCD solute, will change and the interpretation of viscosity measurements on such inhomogeneous fluids is completely unsure.

The claim of Angelini *et al.* [10] of the observation of a first-order phase transition between to fluid phases is therefore not supported by the measurements.

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