

Reply to “Comment on ‘Phase diagram of a solution undergoing inverse melting’ ”

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In their comment, Plazanet, Johnson, and Trommsdorff [Phys. Rev. E 79, 053501 (2009)] point out inconsistencies of our work [Angelini, Ruocco, and De Panfilis, Phys. Rev. E 78, 020502(R) (2008)] with previous measurements performed in solutions composed of α -cyclodextrin, water, and 4-methylpyridine. In particular, they state that the phase transition observed between two fluid phases is simply due to a loss of solubility of the solutions. In this reply, we underline that our work, on the contrary, represents an extension in concentration and temperature ranges with respect to previous studies and that, how explicitly discussed in the same work, the most intimate nature of the high temperature fluid phase has never been defined homogeneous as objected to in the comment.

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The comment by Plazanet, Johnson, and Trommsdorff (PJT) concerns one of the results of our work [1], i.e., the observation of a first-order phase transition between two fluid phases in solutions composed of α -cyclodextrin (α CD), water, and 4-methylpyridine (4 MP). In particular, they “point out inconsistencies with previous measurements, which show that the two fluid phases are not homogeneous liquids” and state that “the claimed phase transition signals simply the loss of solubility of α CD at the transition temperature.” In this work, we propose a temperature-concentration phase diagram for solutions of α CD, water, and 4 MP using differential scanning calorimetry (DSC), rheological methods, and x-rays diffraction, extending the concentration and temperature ranges with respect to previous studies.

We recall here that in the high α CD concentration range ($c \geq 150$ mg/ml), two different fluid phases are separated by a solid region. (The different structures of the solid region were studied in Ref. [2].) The high-temperature points of the phase diagram locate the temperatures (for each concentration) at which the solid phase remelts in the high-temperature

fluid (HTF) which is a disordered fluid phase. This remelting was cited in Ref. [3] for the solution 200 mg/ml, but up to now a systematic study of the remelting temperatures as a function of concentration was never reported. Upon decreasing α CD concentration, we report a shrinking of the solid phase region until a first-order phase transition between two different fluid phases is observed. Here we utilize the modern classification scheme, following which a first-order phase transition involves a latent heat. Our measurements show also the evolution of the DSC thermograms from the low to the high-concentration region providing a connection between the apparently discordant one peak DSC measurement ($c=100$ mg/ml) reported in Ref. [4] and the three peaks DSC thermogram shown in Ref. [2] (see Fig. 1).

On the light of what is summarized, we believe that our work has not been completely understood by PJT, as they focus on the homogeneity of the HTF without considering the relevance of the work in its completeness. To clarify this last point, we underline that we ourselves are fully aware on the issue of the homogeneity of the HTF as clearly stated on page 3 [1]: “These results therefore stimulate further experi-

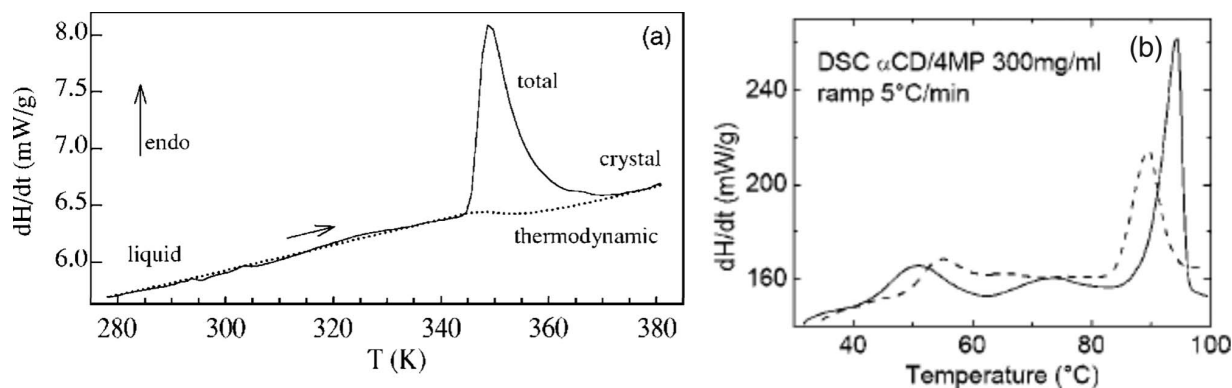


FIG. 1. (a) From Ref. [4]: the rate of heat-flow dH/dt measured during heating the liquid from 278 to 383 K at 12 K/h; (100 mg/ml solution). Reprinted with permission from E. Tombari, C. Ferrari, G. Salvetti, and G. P. Johari, J. Chem. Phys., 123, 051104, (2005). Copyright 2005, American Institute of Physics. (b) From Ref. [2]: differential scanning calorimetry scans of two samples of 300 mg/ml α CD in 4 MP/ H_2O . Reprinted with permission from M. Plazanet, M. Dean, M. Merlini, A. Hüller, H. Hemerich, C. Meneghini, M. R. Johnson, and H. P. Trommsdorff, J. Chem. Phys. 125, 154504 (2006). Copyright 2006, American Institute of Physics.

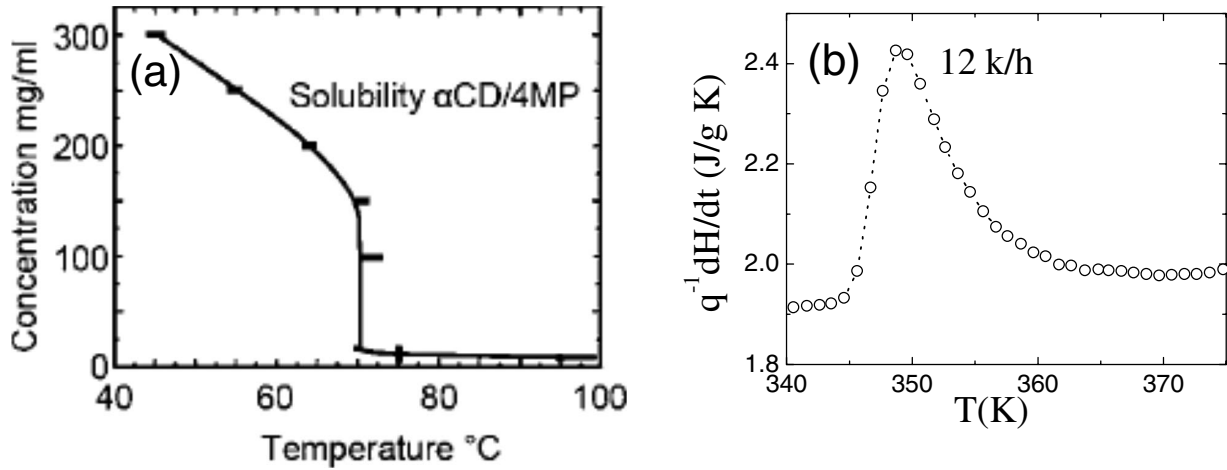


FIG. 2. (a) From Ref. [2]: solubility of α CD in solutions of 4 MP containing approximately 2% in weight H_2O . Reprinted with permission from M. Plazanet, M. Dean, M. Merlini, A. Hüller, H. Hemerich, C. Meneghini, M. R. Johnson, and H. P. Trommsdorff, *J. Chem. Phys.* **125**, 154504 (2006). Copyright 2006, American Institute of Physics. (b) From Ref. [4]: the rate of heat-flow dH/dt divided by the heating rate $q=dT/dt$ is plotted against the temperature, at the indicated heating rate; (100 mg/ml solution). Reprinted with permission from E. Tombari, C. Ferrari, G. Salvetti, and G. P. Johari, *J. Chem. Phys.*, **123**, 051104 (2005). Copyright 2005, American Institute of Physics.

mental and theoretical investigations. In particular, a point which needs to be assessed and which cannot be excluded on the basis of the present measurements is the presence of a phase separation in the HTF” and further on in the text “Specifically, it is important to assess whether the HTF is homogeneous or is a manifestation of a phase separation. This point calls for further experimental and simulation works aiming to understand the interacting mechanism leading to such phenomenology.”

Concerning the phase transitions at high concentrations Plazanet *et al.* [3] in 2004 first discussed their observations in terms of “freezing on heating,” while a little later they explained the same process in terms of solidification due to a loss of solubility [2]. From a thermodynamical point of view, these two observations are quite different and it is possible that this point deserves further investigations and discussions to better understand the phenomenon.

With respect to the concentration $c=100$ mg/ml, in their comment, PJT states that “The observations that crystals are formed upon heating in solutions with molar ratios 1:6:100 α CD: H_2O :4 MP (corresponding to 100 mg/ml α CD) are in

clear contradiction with the claim of Angelini *et al.* [1] that....” We wish to clarify this point. Looking at the solubility plot from Ref. [2] (see Fig. 2), one easily observes that a drop of solubility appears at $c=100$ mg/ml and $T \sim 75$ °C, while in the DSC measurements shown in Ref. [4], the endothermic peak at $c=100$ mg/ml and $T \sim 349$ K is attributed to a liquid-crystal transition. In our Reply, we do observe the same endothermic peak already measured by Tombari *et al.* [4], but we just provide a different explanation of the phenomenon. Our interpretation is also confirmed by the $S(Q)$ which does not show any diffraction peak [1]. We do agree with PJT then that this transition does exist, but in our opinion it occurs between two fluids and not between a liquid solution and a crystalline solid. The nature of the HTF is compatible with a phase separation though. We would like to stress once more that this has never been excluded in the manuscript. On the contrary, this is explicitly discussed in the text, while the most intimate nature of the HTF has never been defined homogeneous as objected in the comment. We believe therefore that the issue must be still a matter of discussion and it deserves further investigations to be deeply understood.

[1] R. Angelini, G. Ruocco, and S. De Panfilis, *Phys. Rev. E* **78**, 020502(R) (2008).
 [2] M. Plazanet, M. Dean, M. Merlini, A. Hüller, H. Hemerich, C. Meneghini, M. R. Johnson, and H. P. Trommsdorff, *J. Chem. Phys.* **125**, 154504 (2006).

[3] M. Plazanet, C. Floare, M. R. Johnson, R. Schweins, and H. P. Trommsdorff, *J. Chem. Phys.* **121**, 5031 (2004).
 [4] E. Tombari, C. Ferrari, G. Salvetti, and G. P. Johari, *J. Chem. Phys.* **123**, 051104 (2005).