Title
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Authors
Pfohl, O.
Hino, T.
Prausnitz, John M.

Publication Date
1994-05-01

LBL-35588
UC-401
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL SCIENCES DIVISION

Submitted to Fluid Phase Equilibria

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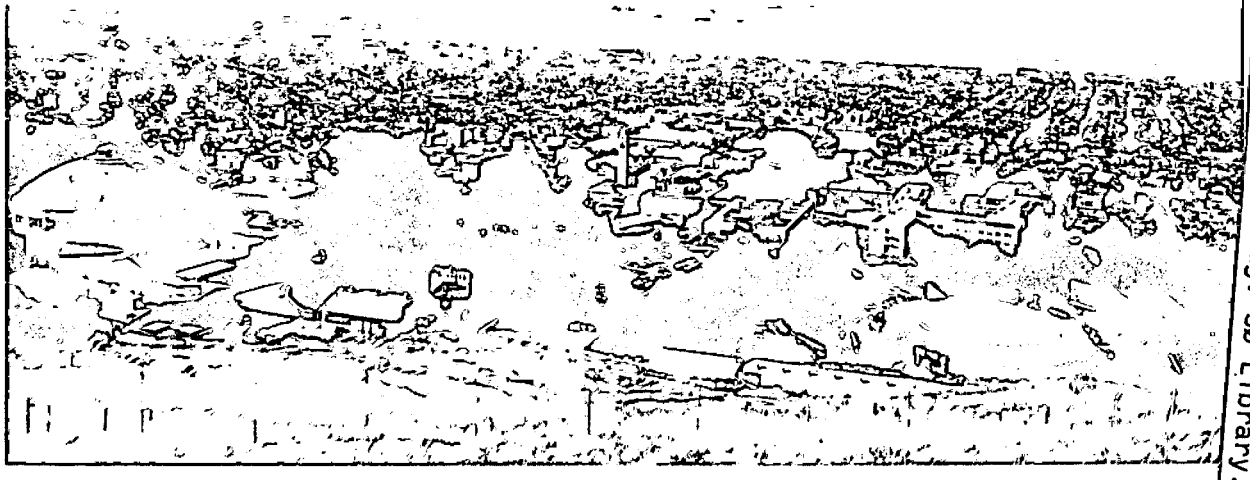
May 1994



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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LBL-35588
UC-401

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Oliver Pfohl, Toshiaki Hino and John M. Prausnitz

Department of Chemical Engineering
University of California
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720, U.S.A.

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098. Additional funding was provided by E. I. du Pont de Nemours & Co. (Philadelphia, PA) and Koninklijke Shell (Amsterdam, The Netherlands).

BRIEF COMMUNICATION

ON THE TEMPERATURE CALIBRATION OF A THERMOOPTICAL APPARATUS

Oliver Pfohl[†], *Toshiaki Hino, and John M. Prausnitz*[*]

Department of Chemical Engineering
University of California, Berkeley
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

ABSTRACT

Saraiva *et al.* (1993) reported lower-critical-solution-temperature data for the system poly(ethylene glycol)/water; they noted a systematic temperature difference of about 3°C when comparing their data with those of Bae *et al.* (1991), even though both groups used the same thermo-optical analysis apparatus and nearly the same chemicals. This difference is shown to be mainly due to poor temperature calibration in a heating chamber with temperature gradients. Presented here are a better calibration method and an easy way to minimize these temperature gradients.

[†] Technische Universität Hamburg-Harburg, Arbeitsbereich Thermische Verfahrenstechnik, Eißendorfer Straße 38, 21073 Hamburg, Germany

[*] to whom correspondence should be addressed

INTRODUCTION

Bae *et al.* (1991) measured cloud-point curves for polymer solutions using a thermooptical analysis (TOA) apparatus consisting of a Mettler Thermosystem with a Mettler FP82 heating-cooling microscope stage (FP82 hotstage) and small glass tubes (i.d.=1 mm and o.d.=3 mm). A similar TOA apparatus with an identical hotstage was used by Saraiva *et al.* (1993) who obtained cloud-point curves for poly(ethylene glycol)/water (PEG/water) systems of various molecular-weight distributions. The TOA apparatus by Bae *et al.* and that by Saraiva *et al.* require only a very small amount of sample (0.02-0.1 cm^3) and yield rapid measurements.

The FP82 hotstage is designed for the thermooptical analysis of substances placed between a slide and a cover glass as used in microscopy (Mettler-Toledo AG, 1984 and 1991). Figure 1a shows a schematic of the heating chamber inside the FP82 hotstage with a slide sample. The sample is placed on the lower heating plate, while the upper heating plate is not in contact with the sample. The temperature indicator is located inside the lower heating plate.

As shown in Figure 1b, Bae *et al.* (1991) placed two copper blocks between the heating plates to use a tube sample in the FP82 hotstage, in such a way that the copper blocks are in contact with the sample tube and both heating plates (Bae, 1994). On the other hand, Saraiva *et al.* (1993) placed a sample tube between upper and lower heating plates without using copper blocks (Saraiva, 1994). Both Bae *et al.* and Saraiva *et al.* checked temperature calibration by measuring the melting points of calibration standards placed between a slide and a cover glass. Both sets of authors implicitly assumed that, in cloud-point measurements where tube samples are used, the temperature of a polymer solution in a tube is the same as that of a calibration standard placed between a slide and a cover glass (Bae, 1994; Saraiva, 1994).

The cloud-point temperatures of the LCST branch in PEG/water systems measured by Saraiva *et al.* are about 3°C lower than those measured by Bae *et al.*, using

nearly identical polymers. The purpose of this note is to show that this systematic discrepancy between these two data sets is mainly due to the presence of a temperature gradient between the heating plates in the absence of copper blocks.

In this work we report the measured melting points (T_m) of benzophenone, benzoic acid, and caffeine, the nematic-isotropic phase transition temperature (T_{NI}) of 4,4'-di-methoxyazoxybenzene (*p*-azoxyanisole, a liquid crystal), and cloud-point temperatures of a PEG/water system at a fixed composition. Three sets of measurements were made for samples placed in the hotstage under the following conditions: first, between a slide and a cover glass; second, in a quartz glass tube with additional copper blocks; and third, in a quartz glass tube without copper blocks. A noticeable difference was observed between the measured transition temperature of a material placed between a slide and a cover glass and the measured transition temperature of the same material placed in a tube in the absence of copper blocks. The difference is caused by a temperature gradient inside the FP82 hotstage. The presence of copper blocks was found to reduce this temperature gradient significantly.

EXPERIMENTAL SECTION

Row 1 of Table 1 gives transition temperatures T_m and T_{NI} of calibration standards supplied by the manufacturers. PEG (M_W=8498, M_W/M_n~1.14) was obtained from Aldrich (Milwaukee, WI). The filled sample tubes were prepared as follows. A syringe filled with solid standard was first heated above the melting temperature of the standard in a vacuum oven. The molten standard was then introduced into a preheated sample tube which was already sealed by flame at one end. The other end of the tube was sealed with a Swagelok cap, a sealing method introduced by Saraiva *et al.* (1993). Measurements with unsealed tubes gave identical results but lead to evaporation and degradation of the samples. The PEG/water solution was prepared at a polymer weight fraction (w_p) of 0.1008. The sample tube was sealed with a flame while the end of the

tube with the polymer solution was immersed in liquid nitrogen. One series of experiments was carried out using another sample tube sealed with a Swagelok cap, the sealing method used by Saraiva *et al.* There was little difference between the measured cloud-point temperatures of the PEG/water sample sealed by flame and those of the sample sealed with a Swagelok cap. Saraiva *et al.* used a Swagelok Union and a metal rod to seal the tubes while we used a Swagelok cap, which should make no difference. Nylon ferrules were used by both groups (Saraiva, 1994).

The details of our TOA apparatus are presented by Bae *et al.* (1991). Like Saraiva *et al.*, we used a FP82 HT hotstage while Bae *et al.* used the older FP82 model. The only noticeable difference between them is the maximum allowable temperature (375 and 300°C, respectively). In this work a one-pound weight was placed on the lid of the FP82 hotstage with the upper heating plate inside to achieve good contact between heating plates, copper blocks and sample tube. In addition, a video camera was attached to the microscope to allow visual inspection of the sample through a monitor. T_m and T_{NI} are the temperatures at which the last crystal or nematic phase were seen by visual inspection through a video camera upon heating. Cloud-point temperatures for the PEG/water system were also determined by visual inspection.

RESULTS AND DISCUSSION

Table I gives the measured T_m and T_{NI} of calibration standards placed in the hotstage under the following three conditions: between a slide and a cover glass; in a quartz glass tube with additional copper blocks; and in a quartz glass tube without copper blocks. In these measurements, the temperature was raised by 0.1°C every 5 to 10 min. Each temperature is an average of at least four measurements on two different samples, except the results for benzophenone which are the averages of at least two measurements on one sample. The results shown in Table I indicate that there is a noticeable difference between the temperature of calibration standards placed between a slide and a cover glass

and the temperature of those placed in a tube in the absence of copper blocks. In addition, the difference of 1.3°C between the measured melting point of caffeine on a slide and that in a tube using copper blocks indicates that it may be necessary to perform temperature-calibration at elevated temperatures using tube samples even if using copper blocks.

The difference between the measured T_m and T_{NI} on tube samples with copper blocks and those without copper blocks was consistently found at various heating rates. Figure 2 compares T_{NI} of the liquid crystal *p*-azoxyanisole in a tube with copper blocks to that without copper blocks measured at different heating rates: observed T_{NI} without copper blocks is about 2°C lower than that with copper blocks at all heating rates accessible with the FP82 hotstage.

Figure 3 shows cloud-point temperatures for a PEG/water system (w_p=0.1008) measured at different heating rates with and without copper blocks. This system exhibits a closed-loop type phase diagram having a lower critical solution temperature at about 125 °C (Bae *et al.*, 1991). The temperatures measured without copper blocks are again about 2°C lower than those observed with copper blocks. The standard deviation of our measurements is about 0.2 °C.

One further series of experiments was carried out in the absence of copper blocks and without the additional weight holding down the lid of the FP82 hotstage. In the absence of a weight on the hotstage lid, the sample tube is not in good contact with the heating plates. Our data show that measurements are sensitive to whether or not the sample tube is in good contact with the heating plates when working without copper blocks. Saraiva *et al.* (1993) used a clamp to hold down the lid of the hotstage which can be assumed to have an influence similar to that of our weight (Saraiva, 1994). Figure 3 shows that Saraiva *et al.*'s data are between ours using the hotstage without copper blocks either with or without a weight for providing good thermal contact.

The temperature of a sample on a slide is different from that in a tube in the absence of copper blocks because the temperature of the upper heating plate in the

hotstage is a few degrees higher than that of the lower plate. Using a thermocouple, temperatures of 149.8±0.2 and 159.2±0.7°C were measured on the surfaces of the lower and upper heating plates, respectively, when the Mettler Thermosystem was set at 150°C. Copper blocks reduce the temperature gradient between heating plates significantly: with copper blocks, the corresponding temperatures are respectively: 149.9±0.1 and 150.5±0.2°C.

When the Mettler FP82 hotstage is used for TOA measurements of polymer solutions in tubes without using additional copper blocks between heating plates, it is necessary to use temperature-calibration obtained with standards placed in a tube.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE–AC03–76SF0098. Additional funding was provided by E.I. du Pont de Nemours & Co. (Philadelphia, PA) and Koninklijke Shell (Amsterdam, The Netherlands). For financial support O. Pfohl also thanks the Ernest Solvay Stiftung (Stifterverband für die deutsche Wissenschaft).

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Saraiva, A.; 1994. Personal communication

TABLE I. Measured Melting and Nematic-Isotropic Transition Temperatures of Calibration Standards in °C

Standard / Condition	Benzophenone (Mallinckrodt) T_m=47~48	Benzoic Acid (Baker) T_m=123	*p*-azoxyanisole (Aldrich) T_{NI}=136	Caffeine (Sigma) T_m=236.5
Slide	48.1±0.1	122.3±0.1	134.1±0.3	236.4±0.2
Tube with copper blocks	48.0	122.3±0.1	134.9±0.2	235.1±0.5
Tube without copper blocks	47.0	117.5±0.4	132.3±0.4	228.7±1.2

T_m=melting temperature

T_{NI}=nematic-isotropic transition temperature

FIGURE CAPTIONS

Figure 1. (a) Schematic of heating chamber in Mettler FP82 Microscope Hotstage with a slide sample. (b) Heating chamber with copper blocks and a tube sample. There are no spaces between heating plates, copper blocks and sample tube. All dimensions are in mm.

Figure 2. Nematic-Isotropic transition temperature (T_{NI}) of *p*-azoxyanisole in tube samples with and without additional copper blocks measured at different heating rates.

Figure 3. Cloud-point temperatures of PEG/water systems (M_W=8498, M_W/M_n~1.14, w_p=0.1008) measured at different heating rates in the presence or absence of copper blocks. (Δ) data from Saraiva *et al.* (M_W=8420, M_W/M_n~1.25, w_p=0.1008) (▲) data from Bae *et al.* (M_W=8000, M_W/M_n~1.6, w_p=0.100).

Figure 1

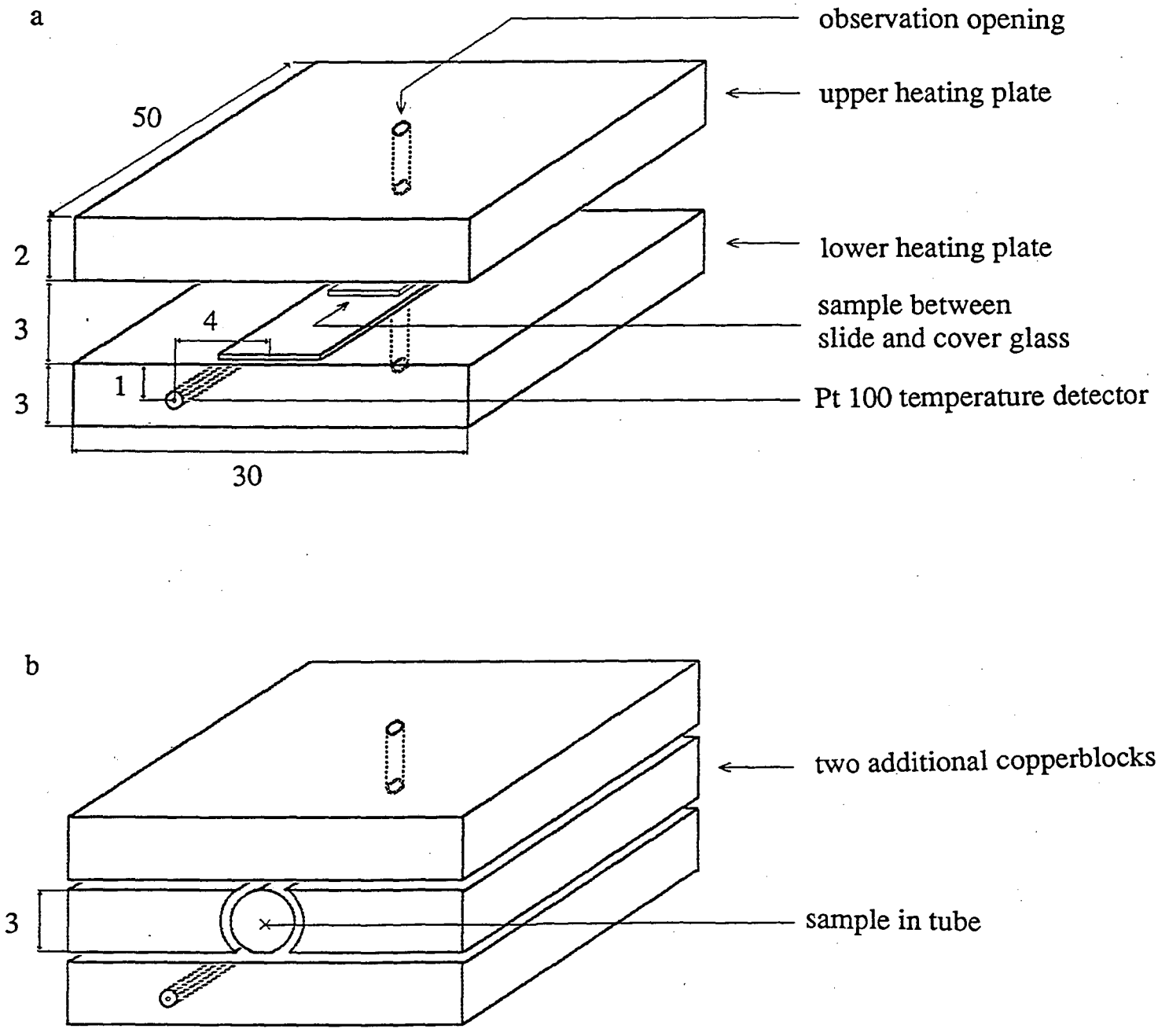

a
observation opening
upper heating plate
50
2
lower heating plate
3
4
sample between
slide and cover glass
1
3
Pt 100 temperature detector
30
b
two additional copperblocks
3
sample in tube

Figure 2

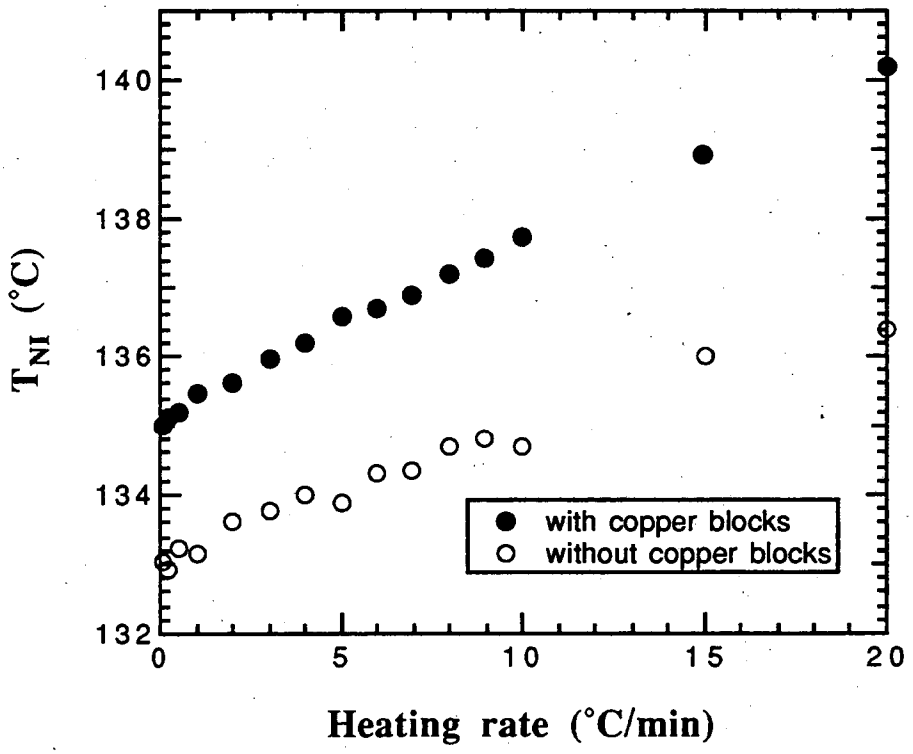
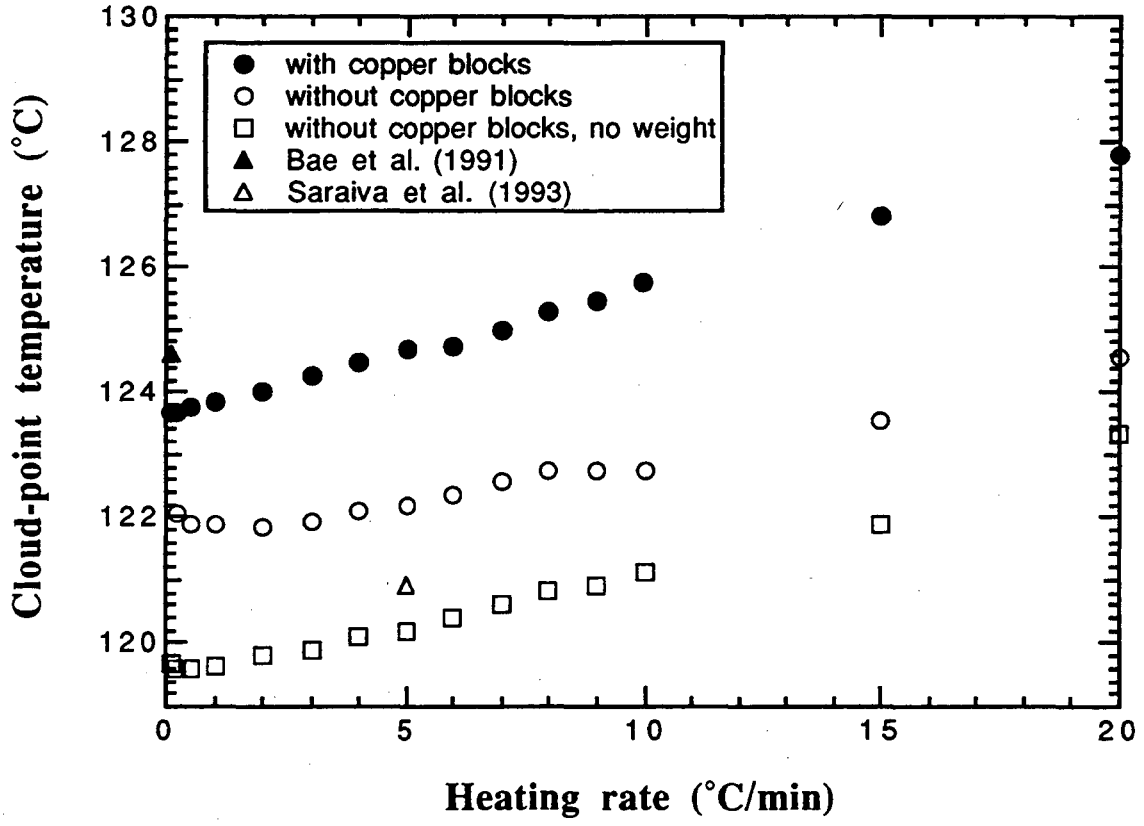

140
138
136
134
132
0
5
10
15
20
T_{NI} (°C)
Heating rate (°C/min)
with copper blocks
without copper blocks

Figure 3


with copper blocks
without copper blocks
without copper blocks, no weight
Bae et al. (1991)
Saraiva et al. (1993)
Cloud-point temperature (°C)
Heating rate (°C/min)
130
128
126
124
122
120
0
5
10
15
20

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