Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

REALIZATION OF THE GLASSY STATE OF SOME SIMPLE LIQUIDS BY THE VAPOR CONDENSATION METHOD

O. HAIDA, H. SUGA AND S. SEKI
Laboratory of Chemical Thermodynamics, Faculty of Science, Osaka University, Toyonaka 560, Osaka (Japan)

(Received July 1st, 1971)

INTRODUCTION

The realization of the glassy states of methyl alcohol[1] and water[2], which has hitherto been unsuccessful using the usual rapid cooling method, has recently been achieved in this laboratory by use of the vapor condensation method. It was shown that this method is very powerful in realizing the glassy state even in cases where other methods had failed. To investigate further the glass transition phenomena of other simple liquids, we have devised a novel type of DTA apparatus which makes it possible to spray the sample vapor on to the sample holder, maintained at liquid hydrogen temperature. In the present work, chloroform and propene were studied and were found to show new glass transition phenomena.

EXPERIMENTAL

Apparatus

The apparatus used in this investigation is shown in Fig. 1. The copper block, around which is wound the heater wire, is joined to the bottom of the Dewar vessel through a Kovar seal. The sample and reference holders, and the shield between them, are made of sheet copper and are all soldered to the bottom of the block. The temperature of the sample was measured with a chromel p–constantan thermocouple attached to the shield by G.E. adhesive. Another pair of constantan wires is soldered to the center of each holder so that they constitute a copper–constantan thermocouple for ΔT measurement. The sampling capillary tube is made of copper tubing 1 mm in diameter. The holder and the tip of the sampling tube can be inspected through an unsilvered portion at the bottom of the Dewar vessel, so that the position of the end of the sampling tube can be adjusted to point towards the center of the sample holder. The other end of the sampling tube is connected to the sample reservoir via a needle valve.

Procedure

The sample vapor was passed through the needle valve and sampling tube, and deposited onto the sample holder which was chilled by refrigerant in the Dewar vessel. The rate of deposition was monitored by automatic recording of the temperature difference (ΔT) between the two holders caused by the heat of condensation, and was carefully controlled with the needle valve. When the rate was too high, it was found that the heat of deposition was liable to induce crystallization of the deposit. When the deposition of the sample was complete and the refrigerant evaporated off, differential thermal analysis was undertaken. The heating rate was approx. 7 K/min near the liquid hydrogen temperature and approx. 2 K/min at about 100 K.

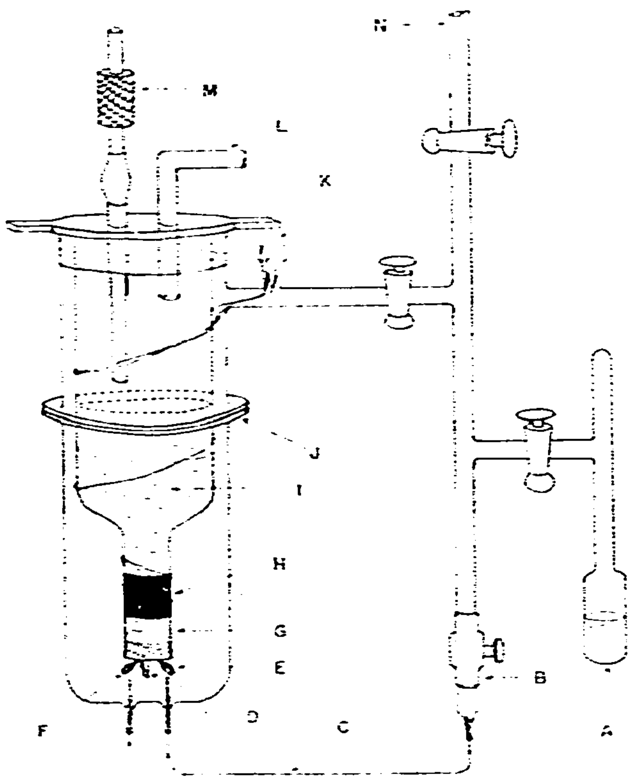

Fig. 1. Schematic diagram of DTA apparatus. A, sample reservoir; B, needle valve; C, sampling tube; D, shield; E, sample holder; F, reference holder; G, copper block; H, Kovar seal; I, refrigerant; J, ground joint; K, leads outlet; L, ventilation; N, to vacuum pump.

Materials

(I). Chloroform

Commercial extra-pure chloroform (Wako Junyaku Co. Ltd.) was purified by the following method. The sample was washed several times with distilled water, dried over calcium chloride, and then purified by fractional distillation. At this stage of purification, the purity as determined by gas-chromatography was ~99.95%. The sample was then distilled twice under high vacuum (10^{-6} mm Hg) and was deaerated carefully under vacuum using a freeze-and-thaw technique.

(2). Propene

Commercial high purity propene (99.9 moles per cent) (Takachiho Chemicals Co. Ltd.) was used without further purification.

RESULTS AND DISCUSSION

Chloroform

Typical DTA curves are illustrated in Fig. 2. Run 1 shows the thermal behavior from 30 to 190°K for the deposit sample prepared at liquid hydrogen temperature.

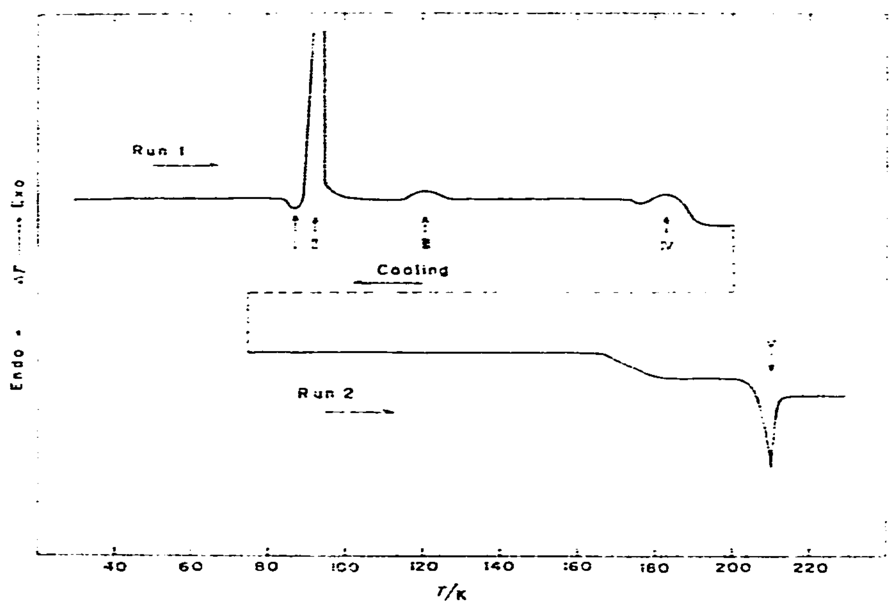

Fig. 2. DTA curves for chloroform.

The small endothermic anomaly begins at 84°K(I) and is followed by a very sharp exothermic peak (II). There are also two broad exothermic anomalies at about 120° (III) and 175°K (IV). As is seen in Run 2, when the temperature cycling was carried out after passing anomaly IV, anomalies I, II, III and IV disappeared in the subsequent warm-up cycle. When the temperature cycling was performed after anomaly II (this case is not reproduced in Fig. 2) anomalies I and II also disappeared. The temperature of 210°K, where the endothermic anomaly occurred, coincides with the literature value for the melting point of this substance. Since the endothermic anomaly I has the general features of the glass transition phenomenon described above, it may be concluded that this anomaly can be attributed to the glass transition and anomaly II to the irreversible phase transition, *i.e.*, crystallization of super-cooled liquid. The crystalline phase, which is produced at this temperature, is transformed to the more stable crystalline forms through exothermic anomalies III and IV. Such a phenomenon is occasionally observed in the case of irreversible crystallization, known as Ostwald's stage law. It is noticeable that the value of the ratio T_g/T_m(= 0.40) is different from the usual one ($\frac{1}{2} \sim \frac{2}{3}$).

Propene

Typical experimental results are given in Fig. 3. Run 1 shows the heating DTA curve of the sample deposited at liquid hydrogen temperature. There are two thermal anomalies at 55–64°K and 64°K. Run 2 shows the process of temperature cycling as in the case of chloroform. The endothermic anomaly at 88°K coincides with the melting point of propene. The endothermic effect at 55°K, which is followed by crystallization of supercooled liquid at 64°K, is attributed to the glass transition phenomenon by the same reasoning as in the case of chloroform.

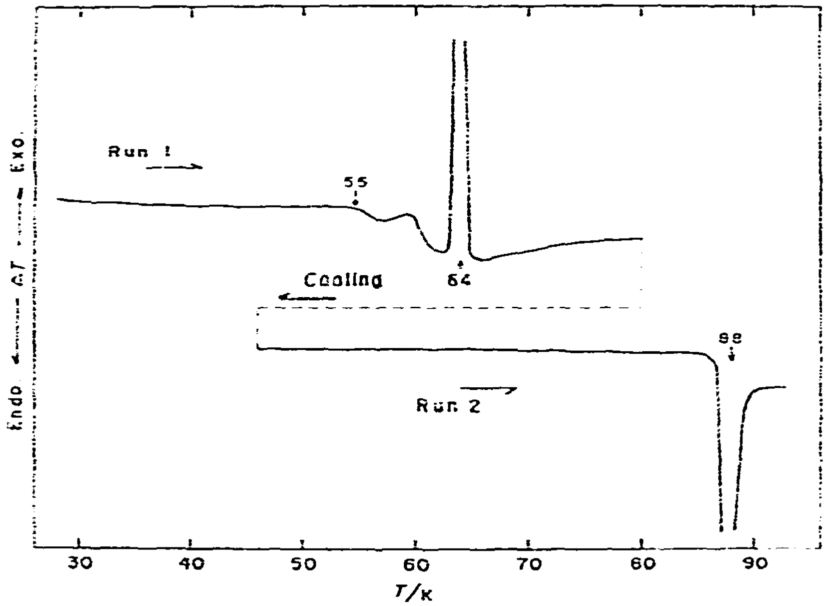

Fig. 3. DTA curves for propene.

REFERENCES

1 M. Sugisaki, H. Suga and S. Seki, *Bull. Chem. Soc. Jap.*, 41 (1968) 2586.
2 M. Sugisaki, H. Suga and S. Seki, *Bull. Chem. Soc. Jap.*, 41 (1968) 2591.