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PHYSICAL PROPERTIES OF ULTRA-PURE PIVALIC ACID

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ABSTRACT

Very high purity pivalic acid has been prepared by repeated distillation and the zone refining technique. Physical properties such as density and viscosity were measured as functions of temperature. Density obeys the expression $\rho = a_0 + a_1 T$, where $a_0 = 1181.8$ kg m^{-3} and $a_1 = 0.8862$ kg m^{-3} K^{-1}, while viscosity shows Arrhenius behavior. Values of η_0 and the activation energy for the viscous flow are 3.459×10^{-3} cP and 4.082×10^{3} cal mol^{-1}, respectively. The volume expansion coefficient was observed to be 9.60×10^{-4} K^{-1}. Heats of fusion and transition were determined by scanning calorimeter, and values observed were 542 ± 11 and 1956 ± 26 cal mol^{-1} respectively. Heat capacity data for the solid and liquid states could be expressed by the equations.

$$C_{p(\text{solid})} = 13.38 + 0.1902T \quad (\text{cal mol}^{-1}\ \text{K}^{-1})$$

and

$$C_{p(\text{liquid})} = 16.19 + 0.1042T \quad (\text{cal mol}^{-1}\ \text{K}^{-1})$$

INTRODUCTION

Glicksman and co-workers [1–3] have been involved in various types of studies conducted on organic plastic crystals, such as solid–liquid interfacial energy measurements, Ostwald ripening, and dendritic crystallization. The presence of impurities causes significant changes to occur in crystallization phenomena. The purification and characterization of the materials were major problems encountered during these studies. Repeated distillation, followed by zone refining under carefully controlled conditions, could achieve the desired ultra-pure materials. The materials under study were molecular plastic crystals, with low melting points, significant vapor pressure in the solid state and low entropies of fusion. Various physical properties, such as viscosity, heats of fusion and transition, densities, and heat capacities in liquid and solid states, are needed to characterize and understand the theoretical and experimental results related to the crystal growth

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phenomena mentioned above. The purpose of the present article is to report selected details of experiments which were carried out for the purposes of determining the equilibrium distribution coefficient, heats of fusion and solid–solid transition, volume expansion coefficient, volume changes during solid–liquid transformation, molar volumes, and the viscosity of ultra-pure pivalic acid near its liquidus temperature.

EXPERIMENTAL

Purification and characterization

Pivalic acid (99%), supplied by Columbia Chemicals, was repeatedly distilled with a Rotovator apparatus under vacuum. The temperature during distillation was maintained between 45 and 50 °C. The final distillate was collected in a tube of 25 mm outer diameter and 75 cm length. The tube was sealed under vacuum and installed on the zone refiner for further purification. The tube was pulled vertically by a geared motor through six sequential ring heaters at a speed of 2.0 cm h^{-1}. The tube was subject to 30 zone-refin-

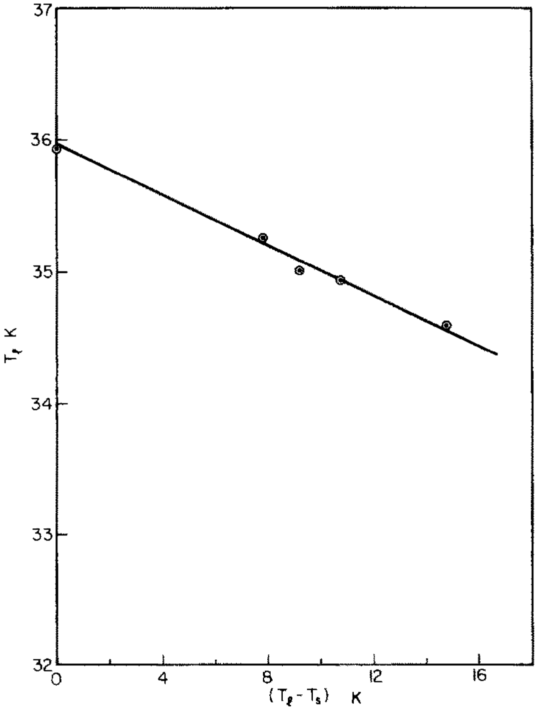

Fig. 1. Plot of liquidus temperature against difference between the liquidus and solidus temperatures.

ing passes. Details are discussed in ref. 4. The characterization of the material was accomplished on the basis of solidus and liquidus measurements. Material near the top was ultra-pure and that near the bottom less pure. Material from different locations was analyzed in a temperature controlled bath. The fluid in the bath was stirred constantly, and the temperature was controlled by a resistance heating element responding to a Tronac temperature controller. The bath could be controlled routinely to ± 0.0003 K over a period of several hours. The liquidus temperature was taken as the temperature at which a small crystal neither grew nor diminished in size. The solidus was chosen as the temperature at which liquid drops appear within the grains of solid. The results are plotted in Fig. 1.

Density and molar volume

Density measurements were carried out in a pycnometer attached to a capillary of 2 mm bore and 20 cm length. The pycnometer was calibrated by filling it with a known mass of distilled water. It was held in a thermostatted bath, and the water level in the capillary was recorded to estimate the sampler volume at different temperatures. The pycnometer was then given a standard glass cleaning procedure followed by a mixture of 4% HF, 36% HNO_3 and 60% distilled water. Traces of the remaining water were driven out by heating for 3–4 h in an oven maintained at 120 ° C. Purified pivalic acid was melted and introduced into the pycnometer, which was again fixed in the thermostatted bath to record the height of liquid in the capillary. For each set of observations, 25–30 min was allowed to attain the temperature of the bath. Results are plotted in Fig. 2 as a function of temperature.

Viscosity measurements

Viscosity was measured as a function of temperature above the melting point of the material. A falling ball (Sargent-Welch V-2100 Gilmont)

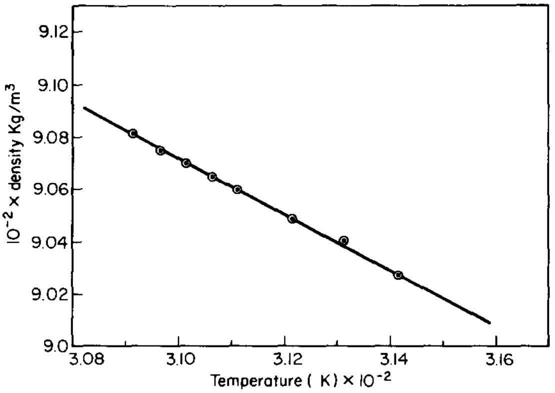

Fig. 2. Graph of density against temperature.

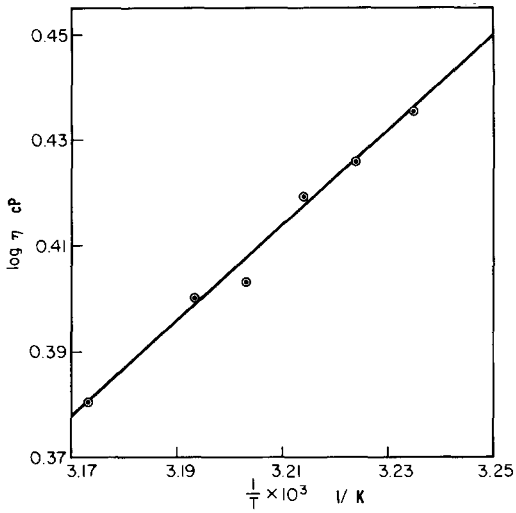

Fig. 3. Plot of log η against T^{-1}.

viscometer filled with the material was kept in the thermostatted bath to record the falling time of the ball. Water was used as reference material to determine the viscosity. The results are plotted in the form of log η and T^{-1} in Fig. 3.

Heats of fusion and transition and heat capacity measurements

A Perkin-Elmer DSC differential scanning calorimeter with computer-aided data acquisition analysis was used to determine the heat of fusion and the heat capacities in solid and liquid states. Samples were prepared in hermetically sealed aluminum pans. All the runs were carried out with a range of 2 m cal s^{-1}, charge speed 5 mm min^{-1} and chart range (100 divisions) 10 mV. For the heat of fusion and solid–solid transition, the heating rate was 1.25 K min^{-1} and for the heat capacity it was 5 K min^{-1}. In the determination of heat capacity the chart recorder speed was 10 mm min^{-1}. Results are given in Table 1 and compared with available data.

DISCUSSION

The purity of pivalic acid can be computed from the depression of the specimen's liquidus temperature T_l using the equation

$$X_A = 1 - \frac{T_0 - T_l}{m_l} \qquad (1)$$

where T_0 is the melting point of the theoretically pure material and m_l is the slope of the liquidus line defined as $\Delta T/\Delta X_A$.

TABLE 1

Results of scanning calorimetry

Property	Experimental value	Literature value [a] [6]
Heat of fusion	542 ± 11 cal mol^{-1}	502.35 cal mol^{-1}
Heat of transition	1956 ± 26 cal mol^{-1}	2093.67 cal mol^{-1}
Heat capacity of solid	43.95 cal mol^{-1} K^{-1}	–
Heat capacity of liquid	48.82 cal mol^{-1} K^{-1}	–
ΔC_p	4.87 cal mol^{-1} K^{-1}	–

[a] These values were for the commercial sample as received.

T_0 was established through measurements of the solidus and liquidus temperatures of the sample at various impurity levels. The melting point of high-purity pivalic acid was 35.935 °C. The value of m_1 can be further calculated from T_0 and the slope β of the experimental curve shown in Fig. 1. Glicksman [5] has derived that

$$\beta = \frac{T_1 - T_0}{T_0 T_s} = \frac{m_1}{m_1 - m_s} \tag{2}$$

$$\frac{T_1 - T_0}{T_1 T_0} = \frac{m_1}{m_1 - m_s} \tag{3}$$

$$m_1 = \frac{R T_0^2}{\Delta H_{\mathrm{f}}(\beta - 1)} \tag{4}$$

Equations (1) and (3) indicate a purity level of 99.9995%. Equation (2) can be written as

$$\beta = \frac{m_1}{m_1 - m_s} = \frac{k}{k - 1} \tag{5}$$

This predicts that the distribution coefficient of impurity in pivalic acid is 8.37×10^{-2}.

Figure 2 shows a linear relationship between density and absolute temperature. For the observed temperature range, density obeyed the expression

$$\rho = a_0 + a_1 T \tag{6}$$

where $a_0 = 1181.8$ kg m^{-3} and $a_1 = -0.8862$ kg m^{-3} K^{-1}. Standard errors for the regression coefficients a_0 and a_1 were 10.37 and 0.03327 respectively. Using eqn. (5), density at the liquidus temperature was found to be 9076.9 kg m^{-3}. The volume expansion coefficient α was evaluated as follows

$$\alpha = \left(\frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}T}\right)$$
$$= \frac{\ln V_2/V_1}{\Delta T} \tag{7}$$

α was found to be 9.60×10^{-4} K^{-1}. The change in the volume during solid–liquid transformation was observed at 35.80 °C to be 4.2%. This indicates that the density of the solid phase at 35.80 °C would be 946.4 kg m^{-3}.

Figure 3 is a straight line plot between log η and T^{-1}, indicating Arrhenius type behavior

$$\eta = \eta_0 \, e^{E/RT} \tag{8}$$

where η_0 is 3.46×10^{-3} cal mol^{-1} and the energy of activation E is 4.082×10^3 cal mol^{-1}. The coefficient of determination in the analysis was 0.9821. Equation (6) predicts that viscosity at the liquidus temperature should be 2.73 cP. Since pivalic acid could not be supercooled sufficiently below the liquidus temperature, it was not possible to determine its viscosity in the supercooled state. In this situation, it is not possible to discuss prefreezing behavior from the viewpoint of molecular ordering, clustering or any other type of association of molecules. The results of scanning calorimetry indicated a solid–solid transition in addition to the solid–liquid transformation. It was also found that there appeared to be some kind of decomposition above 320 K (exothermic drift of trace). Thus a series of runs was done between 250 and 350 K. The heats of fusion and transition were computed using the UTINT2W program. Various types of baseline (slope–slope and point–point) were used over various temperature ranges. For the solid–solid transition, values obtained by different analyses never differed by more than 2%. However, for the heat of fusion runs, the value obtained was very much dependent on how the integration was performed. This is obviously due to exothermic drift above the liquidus temperature. Thus, it was decided to use a point–point baseline for both the solid–solid transition and the heat of fusion runs. This showed that the temperature of solid–solid transition was 278.3 ± 0.2 K. The heat capacities for the solid and liquid states were fitted to the equation

$$C_p = a + bT \tag{9}$$

The values of each run were averaged using the run averaging program for values from 295–300 K and 313–319 K. The standard deviation obtained was 0.6%, and values are given in Table 1. Heat capacity equations for the solid and liquid were

$$C_{p(\text{solid})} = 13.38 + 0.1902T \ (\text{cal mol}^{-1}\ \text{K}^{-1}) \tag{10}$$

and

$$C_{p(\text{liquid})} = 16.19 + 0.1042T \ (\text{cal mol}^{-1}\ \text{K}^{-1}) \tag{11}$$

In each case the fit was within 0.7%. Equations (10) and (11) predict that the heat capacities for the solid and liquid at the liquidus temperature are 45.40 and 48.39 cal mol^{-1} K^{-1}, respectively.

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REFERENCES

1 M.E. Glicksman, R.J. Schaefer and J.D. Ayers, Philos. Mag., 32 (1975) 725.
2 M.E. Glicksman, R.J. Schaefer and J.D. Ayers, Metall. Trans., A, 7A (1976) 1747.
3 M.E. Glicksman and N.B. Singh, J. Cryst. Growth, in press.
4 M.E. Glicksman, N.B. Singh, E. Rubenstein and Q.T. Fang, J. Cryst. Growth, 89 (1988) 101.
5 M.E. Glicksman, N.B. Singh and M. Chopra, unpublished results.
6 E.M. and L. Breed, Thermochim. Acta, 1 (1970) 242.