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Heat capacity of glycerol from 298 to 383 K

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Abstract

The heat capacity, C_p, of glycerol was measured between 298 and 383 K with a DSC and a modulated scanning calorimeter operating at 5 mHz. The two sets of data show an excellent agreement and can be fitted to the equation: C_p (J mol^{-1} K^{-1})=90.983+0.4335T. The C_p values, at 298.15 K, tabulated in literature and in data handbooks agree with the current data, but the equation reported for $C_p(T)$ at higher temperatures is wrong, giving a slope which is ca. 60% of the determined value. © 1998 Elsevier Science B.V.

Keywords: Glycerol; Heat capacity

1. Introduction

In spite of the large amount of thermodynamic data on glycerol, the measurements of the heat capacity, C_p, above the room temperature are scarce. Berthelot [1], in 1879, derived C_p in the 373–468 K range. Subsequently, some Russian researchers measured C_p and Omelchenko [2] in 1962 reviewed their data and expressed the relationship of C_p (J mol^{-1} K^{-1}) vs. T by the equation: $C_p(T)=137.654+0.3184T-0.0001125T^2$. The agreement between the experimental data and the C_p values, calculated from the fitting of equation, was within 1–4%. This equation is quoted in data handbooks and in reference data [3].

The results reported in this study were obtained during experiments planned for testing a new modulated scanning calorimeter (MSC), [4]. The heat capacities of several substances: heptane, water, dodecane, mercury, ethylene glycol and glycerol, were measured at 292.2 K and the experimental values were in good agreement with those reported in the literature. The temperature scanning runs performed with mercury as the unknown sample and ethylene glycol, EG, as the reference material [3], gave data which fitted very well with the linear equation previously reported [5]. In the case of glycerol, an unexpectedly large difference was found between the measured values and those in Ref. [3], particularly at temperatures >323 K. To shed light on this apparent disagreement, further accurate experiments were performed using fresh, anhydrous pure glycerol and, in addition, a Perkin–Elmer DSC. The good agreement between the data obtained with the two different calorimeters

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confirmed that the $C_p(T)$ equation in Ref. [3] is simply wrong.

2. Methods and materials

The MSC is a differential calorimeter, equipped with two twin cells, planned and built following a technique developed a few years ago [6]. The main features of the instrument are:

1. the capability of performing absolute measurements;
2. high sensitivity (±0.001 J/K); and
3. an accuracy which is, in practice, limited by the accuracy of the heat capacity value of the reference material.

The thermodynamic heat capacity of the sample ($\cong$100 mg, weighed within ±0.02 mg), measured in the temperature scanning mode, is given by Eq. (1) which contains the out-of-phase component, $P''(t)$, of the oscillating power, $P(t)$, necessary to nullify the temperature difference between the twin cells. The sample temperature, $T(t)$, is scanned and modulated at the angular frequency ω, as shown in Eq. (2):

$$C_x(\omega, t = n\tau) = \frac{P''_n}{\omega T_m} \quad (1)$$

$$T(t) = T_0 + \beta t + T_m \cos \omega t \quad (2)$$

where $\tau = 2\pi/\omega$ is the modulation period, T_m the modulation amplitude and β the temperature scanning rate [4]. The in-phase component of $P(t)$ gives the imaginary part of the complex heat capacity, which is different from zero when the sample relaxation times are comparable with the modulation period, for example near the glass transition [7]. In the present case, the sample dynamics is always faster than the temperature change rate, so the imaginary part must be null, as actually observed.

Ethylene glycol was adopted as the reference material because its boiling temperature is high, 470.45 K, and its $C_p(T)$ is known in the temperature range of interest [3].

To test, in addition, the quality of ethylene glycol, the $C_p(T)$ of mercury was measured and the results were compared with the data reported in the literature [5]. The good agreement that was obtained was considered as conclusive reliability of the experimental procedure.

The experimental conditions were as follows: the temperature modulation frequency, 5 mHz; the modulation amplitude, 0.25 K; and the scanning rate, 0.15 K/min. The absolute temperature of the sample was known within ±0.1 K.

The second set of data was obtained with a Perkin–Elmer DSC 7 differential scanning calorimeter. The external block temperature control was set at 248 K and dry nitrogen was used as purge gas. The instrument was calibrated with high purity standards (indium, cyclohexane, *n*-octadecane) at a temperature scanning rate of 3 K/min. The temperature was known within ±0.1 K. The samples (10–15 mg) were weighed to ±0.1 mg and encapsulated into hermetically sealed pans. The heat capacity of the sample was obtained with a procedure based on three runs: the sample run, the blank run and the standard (sapphire) run [8]. Care was taken to ensure that, for all the three runs, the initial and final isotherm levels were identical. The heat capacity against T of the sample was calculated by means of the commercial software by Perkin–Elmer. The error, estimated from the analysis of repeated runs, was less than ±1%.

Commercial chemical samples were utilised as received, without further purification. The nominal purities were: ethylene, 99% (Baker); glycerol, anhydrous 99.5%, (Fluka); and mercury, 99.5%, (Carlo Erba).

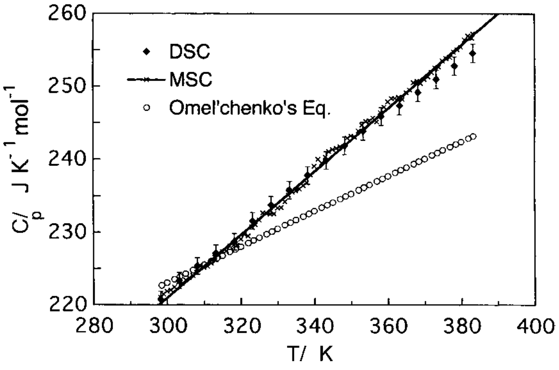

Fig. 1. Comparison of the $C_p(T)$ values of glycerol vs. temperature, obtained by DSC and MSC, with data in literature.

3. Results and discussion

The two sets of experimental data from DSC and MSC, in the 298–383 K range, are shown in Fig. 1. The data points calculated with the equation of Omelchenko [2] are also plotted.

The good agreement between the current C_p values, independently obtained with different calorimeters and procedures, is very apparent. The MSC data points can be fitted to the equation: $C_p(T)=90.983+0.4335T$ from 298 to 383 K. The DSC data at temperatures >363 K were slightly lower. The generally accepted $C_p(T)$ equation [3] is incorrect. At temperatures >323 K, the calculated values were significantly out of the experimental uncertainty of the MSC and DSC.

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