



Liquid glycerol: Experimental densities at pressures of up to 25 MPa, and some derived thermodynamic properties



Nieves M.C.T. Prieto^a, Thiago A. Souza^b, Ana P. Egas^a, Abel G.M. Ferreira^{a,*}, Lélío Q. Lobo^a, António T.A. Portugal^a

^a Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal

^b Universidade Federal Rural do Rio de Janeiro, Brazil

ARTICLE INFO

Article history:

Received 7 February 2016

Received in revised form 13 May 2016

Accepted 14 May 2016

Available online 17 May 2016

Keywords:

Glycerol
Density
Equation of state
Vapour pressure
Enthalpy of vapourisation

ABSTRACT

In spite of the importance of glycerol in industry, only limited consistent information on its *pVT* data seems to be available in the literature. In this work, the density of glycerol (1,2,3-propanetriol) was measured within the temperature range 298.15–348.15 K and over the pressure range from atmospheric pressure up to 25.0 MPa by means of a vibrating tube densimeter. The estimated combined standard uncertainty of measurements is $0.86 \text{ kg}\cdot\text{m}^{-3}$. The experimental *pVT* values of this study combined with selected values from the literature covering the ranges of $T = (278\text{--}373) \text{ K}$ and of $p = (0.1\text{--}200) \text{ MPa}$ were fitted using the Goharshadi–Morsali–Abbaspour equation of state (GMA EoS). The measured density in this work correlates with deviations of $\pm 0.05\%$ (less than $0.5 \text{ kg}\cdot\text{m}^{-3}$) and in the range $\pm 0.1\%$ with the overall results. From the GMA EoS, the mechanical coefficients as thermal expansivity, isothermal compressibility and internal pressure were calculated. Vapour pressures selected from the literature covering the temperature range between the triple point and the normal boiling point were correlated with the Wagner equation. This equation was used in conjunction with the Clapeyron equation to calculate the molar enthalpies of vapourisation from the triple point to the normal boiling point.

© 2016 Elsevier Ltd.

1. Introduction

The density of liquid glycerol (1,2,3-propanetriol) has been measured since the early years of the eighties in the nineteenth century but the experiments carried out by Bridgman [1] were the first ones covering extensive temperature ranges and made up to high pressures. In spite of the importance of glycerol both on theoretical and practical grounds, only a few consistent studies on density have been published since that pioneering work. Moreover, much of the information available for the density of the liquid at atmospheric pressure is fragmentary and derives from studies on binary mixtures [2]. This led us to make measurements of this property from 298.15 K to 348.15 K and pressures of up to 25 MPa using a vibrating tube densimeter. The existing data in the literature were also assessed and those considered the most reliable were combined with our own measurements and treated by using the equation of state due to Goharshadi–Morsali–Abbaspour (GMA EoS) [3]. This equation of state has been found to be adequate for polar, non-polar, and H-bonded fluids. Some of the

mechanical coefficients of the liquid such as the thermal expansivity, the isothermal compressibility, and the internal pressure were calculated from the equation of state and compared with values from the literature.

In addition to the density of the liquid, the development of chemical processes involving glycerol often requires the knowledge of accurate vapour pressure data and of the enthalpy of vapourisation. Due to the very strong molecular association in the liquid phase, glycerol has a lower vapour pressure than would be expected from its molar mass. Accurate values of vapour pressure for glycerol are scarce and those existent lie in the micron range ($<10^{-3}$ torr), usually measured by effusion techniques, are inconsistent. The values for vapour pressures higher than 1 kPa have often been obtained from ebulliometry or using static apparatus. In this work, reliable vapour pressures selected from the literature, including the critical point coordinates measured by Nikitin et al. [4], were correlated by using the well-known Wagner equation [5]. The values of the enthalpy of vapourisation were also evaluated from the triple point temperature to the normal boiling temperature.

* Corresponding author.

E-mail address: abel@eq.uc.pt (A.G.M. Ferreira).

2. Experimental

2.1. Chemicals

Glycerol was obtained from Sigma–Aldrich (CAS number 56-81-5) with stated mass fraction purity (GC) ≥ 0.995 (water by Karl Fisher ≤ 0.001). Since glycerol is highly hygroscopic, samples were degassed ultrasonically, dried over freshly activated molecular sieves (Type 3 Å) supplied by Aldrich and further purified by evaporation in a rotary evaporator working at 343 K. The water content was determined with a Metrohm 831 Karl Fisher coulometer indicating that the purification procedure reduced the water mass fraction from 1.3×10^{-3} to 7×10^{-4} .

2.2. Density measurements

Liquid densities were measured using an Anton Paar DMA 60 digital vibrating tube densimeter with a DMA 512P measuring cell, within the temperature range from 298.15 K to 348.15 K and over pressures from 0.10 MPa to 25.0 MPa. The measuring setup and the calibration of the vibrating tube densimeter were described in detail in a previous paper [6]. The temperature in the vibrating tube cell was measured with a platinum resistance probe with standard uncertainty $u(T) = 0.01$ K. The probe was previously calibrated over the range 273.15–373.15 K against a platinum resistance thermometer ERTCO-Eutechnics High Precision Digital Thermometer certified in the ITS90. A Julabo F12-ED thermostatic bath with ethylene glycol as circulating fluid was used in the thermostat circuit of the measuring cell held constant to ± 0.01 K. The required pressure was generated and controlled with a Pressure Generator model 50-6-15, High Pressure Equipment Co., using acetone as hydraulic fluid. The diameter of the metallic tube used in the measurements was 1.59 mm, the buffer being longer than 1 m to guarantee the inexistence of back diffusion of the hydraulic liquid into the liquid contained in the densimeter cell. Pressures were measured with a pressure transducer (Wika Transmitter S-10, WIKA Alexander Wiegand GmbH & Co.) with a maximum standard uncertainty of $u(p) = 0.03$ MPa. An NI PCI-6220 data acquisition board (DAQ) from National Instruments (NI) was used for the real time registration period, temperature, and pressure values. For this task, a Labview application was developed. Modules of temperature (NI SCC-FT01) and pressure (NI SCC-CI20) were installed in a NI SC-2345 carrier and connected to a DAQ board. Taking into account four values of the period of oscillation at every (T, p) state the precision of the density measurements is of the order of $\pm 0.1 \text{ kg}\cdot\text{m}^{-3}$.

The influence of viscosity on the density uncertainty (due to damping effects on the vibrating tube) can be of some importance in liquid glycerol because of the high values of that property in the range of the density measurements. For liquids with viscosities less than 100 mPa·s this uncertainty can be obtained by using an equation given by the Anton Paar suppliers [7] for the DMA512P densimeter.

$$\Delta\rho/\rho = (-0.5 + 0.45\sqrt{\eta}) \cdot 10^{-4} \quad (1)$$

where ρ represents the density value obtained from the DMA512P densimeter, $\Delta\rho$ is the difference between this density value and the corrected density due to the effect of the viscosity of the liquid, and η is the dynamic viscosity (in mPa·s). For viscosities higher than 400 mPa·s, the viscosity correction factor becomes constant and equal to $0.5 \text{ kg}\cdot\text{m}^{-3}$ [8]. Between (100 and 400) mPa·s, the viscosity correction shows intermediate behaviour. From the measured densities in this work and the viscosities at atmospheric pressure measured by Shankar and Kumar [9] and Cook et al. [10] over the overall temperature range from 273.15 K to 398.15 K, the uncertainty in

density due to viscosity is about $0.5 \text{ kg}\cdot\text{m}^{-3}$ at temperatures lower than 308.15 K, and $0.3 \text{ kg}\cdot\text{m}^{-3}$ for higher temperatures. The combined standard uncertainty of the density measurements, estimated taking into account the influence of uncertainties associated with calibration equation [6], temperature, pressure, period of oscillations (six-digit frequency counter), viscosity, and density data of calibrating fluids was $u_c(\rho) = 0.86 \text{ kg}\cdot\text{m}^{-3}$. The expanded uncertainty with confidence level 95% (coverage factor $k = 2$) was estimated to be $U(\rho) = 1.7 \text{ kg}\cdot\text{m}^{-3}$.

3. Results and discussion

3.1. Fixed points and sources of data

For the normal melting temperature of glycerol, Wilhoit et al. [11] selected the value $T_m = (291.8 \pm 0.2)$ K reported by Volmer and Marder [12] who made the measurements by carefully protecting a dry sample from atmospheric moisture. This value has been given as the triple point temperature T_p by NIST [13] and was considered as such in the present work. The only measurements of the critical temperature T_c and critical pressure p_c have been made by Nikitin et al. [4] who used the method of pulse heating a wire probe placed in the liquid obtaining $T_c = 850$ K and $p_c = 7500$ kPa. For unstable decomposing liquids as glycerol, they found that the critical temperature depends on the heating time. The extrapolation of duration of heating for zero gives $T_c = 850$ K. The critical temperature and pressure presented by Nikitin et al. [4] were selected for this work and they can be compared with the values $T_c = 726$ K, and $p_c = 6680$ kPa tabulated by Reid et al. [14]. These authors have selected $T_b = 563.15$ K as the temperature at the normal boiling point and this value is usually used in reference works.

The density studies over wide ranges of temperature and pressure can be summarized as follows. Bridgman [1] used a variable-volume cell with bellows and used the density of liquids at 273.15 K as reference to obtain fractional changes of volume. McDuffie et al. [15] developed a variable-volume cell with bellows and the densities of pressurized liquid were found from measured values at atmospheric pressure. This author did not provide the measured values of density giving instead the graphical representation of data with Tait equation of state. Khelladi et al. [16] used a vibrating U-tube densimeter to make the density measurement of density as function of temperature at atmospheric pressure. They used these values and the experimental measurements of speed of sound in the range 283–373 K and pressures up to 100 MPa combined with the heat capacity at atmospheric pressure to calculate the density at those ranges of temperature and pressure applying an iterative technique. Khelladi et al. [16] compared their calculated density results with the values from Tait EoS reported by Cibulka et al. [17] and deviations lower than 0.2% (less than $3 \text{ kg}\cdot\text{m}^{-3}$) were found. Some few indirect determinations of density as a function of pressure come from experimental compressions made by Nakagawa et al. [18], by Miyamoto et al. [19] and by Egorov and Makarov [20]. Walsh and Rice [21] and Dick [22] reported densities at very high pressures. Extensive data at atmospheric pressure (determinations in temperature ranges of 50 K length or more) come from Adamenko [23], Khelladi et al. [16], Egorov and Makarov [24] and Egorov et al. [2].

The density values for glycerol measured in this work are reported in Table 1 and plotted in Fig. 1 as a function of pressure and temperature. All the experimental values show that density has the expected behaviour with the temperature and pressure: the increase with pressure for isothermal conditions and the drop of density as temperature increases at fixed pressure. Another conclusion is that the purification process of glycerol had no influence

Download English Version:

<https://daneshyari.com/en/article/214932>

Download Persian Version:

<https://daneshyari.com/article/214932>

[Daneshyari.com](https://daneshyari.com)