Fluid Phase Equilibria 315 (2012) 64–76

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Experimental study of the density and viscosity of polyethylene glycols and their mixtures at temperatures from 293 K to 465 K and at high pressures up to 245 MPa

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ARTICLE INFO

Article history:
Received 7 September 2011
Received in revised form
15 November 2011
Accepted 20 November 2011
Available online 28 November 2011

Keywords:
Density
Diethylene glycol
Monoethylene glycol
Tait-type equation of state
Triethylene glycol
Viscosity

ABSTRACT

Density and viscosity of monoethylene glycol (MEG), diethylene glycol (DEG), and triethylene glycol (TEG) and their binary, (50%MEG + 50%DEG), (50%MEG + 50%TEG), (50%DEG + 50%TEG), and ternary (33.33%MEG + 33.33%DEG + 33.34%TEG) mixtures have been simultaneously measured over the temperature range from 293 K to 465 K and at pressures up to 245 MPa using the hydrostatic weighing and falling-body techniques. The expanded uncertainty of the density, pressure, temperature, and viscosity measurements at the 95% confidence level with a coverage factor of $k = 2$ is estimated to be 0.15–0.30%, 0.05%, 0.02 K, and 1.5–2.0% (depending on temperature and pressure ranges), respectively. Tait-type equation of state (EOS) for pure MEG, DEG, and TEG has been developed using the measured (p, ρ, T) data. Theoretically based Arrhenius–Andrade and Vogel–Tamman–Fulcher type equation with pressure dependent coefficients was used to describe the temperature dependence of measured viscosities for pure polyethylene glycols.

1. Introduction

In this work we used a new experimental apparatus for simultaneous measurements of the density and viscosity of liquids at high temperatures (from room temperature to 500 K) and at high pressures (up to 250 MPa) based on hydrostatic weighing and falling-body techniques, respectively. In our recent publication [1] we described in detail the construction of the measuring cell, procedure of measurements and uncertainty analyses. In the same paper we reported experimental density and viscosity data for MEG, DEG, and TEG and their binary, (50%MEG + 50%DEG), (50%MEG + 50%TEG), (50%DEG + 50%TEG), and ternary (33.33%MEG + 33.33%DEG + 33.34%TEG) mixtures at temperatures from 293 K to 473 K and at atmospheric pressure. In this work we used the same apparatus to measure density and viscosity of the same compounds at high temperatures from 293 K to 465 K and at high pressures (up to 250 MPa). In our recent publication [1] we provided detailed review of all the available reported experimental density and viscosity data for MEG, DEG, TEG and their binary and ternary mixtures at atmospheric pressure. We also provided detailed comparison from our density and viscosity measurements for these systems at 0.1 MPa using the same apparatus. A survey of the literature shows that no previously reported density data for the pure DEG, TEG and the binary and ternary mixtures of MEG, DEG, and TEG under pressure. Also we did not find any viscosity measurements under pressure for pure MEG, DEG, TEG and their mixtures. For pure MEG very restricted density data are available under pressure. A survey of the literature reveals that there are only four data sources, Wong [2], Guignon et al. [3], Egorov et al. [4], and Bridgman [5], in the literature for the density of MEG under pressure. There are no reported density and viscosity data for other compounds and their mixtures. Wong [2] reported the density measurements for MEG in the very restricted pressure range (up to 7 MPa) and at temperatures from 298 K to 348 K. The measurements were made using VTD. The uncertainty in density measurements was 0.05%. Guignon et al. [3] reported measured densities for MEG at single temperature of 288.22 K and at pressures up to 350 MPa. They also used VTD technique. The uncertainty in specific volume measurements is about 6×10^{-8} m^3 kg^{-1}. The compressibility data ($k = (\rho - \rho_0)/\rho$, where ρ_0 and ρ are the density at atmospheric pressure and at pressure P, respectively) reported by Egorov et al.

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doi:10.1016/j.fluid.2011.11.022

[4] for MEG are cover over the temperature range from 278 K to 323 K and pressure range from 0.1 MPa to 100 MPa. Measurements were performed using constant volume piezometer. The densities of MEG at atmospheric pressure ρ_0 were measured using VTD with the uncertainty of 5×10^{-2} kg m^{-3}. Bridgman [5] reported indirect measured densities of MEG in the temperature range from 273 K to 368 K (along three isotherms of 273 K, 323 K, and 368 K) at high pressures up to 1200 MPa using Bellows volumetry. Steele et al. [6,7] reported saturated liquid densities for DEG and TEG. These measurements are covering the temperature range from 323 K to 498 K for DEG and from 313 K to 473 K for TEG. At these temperature ranges the values of vapor-pressure for these systems are within 0.002–0.168 MPa. Therefore, the present study considerably extended the temperature and pressure ranges of the previous studies and provides new accurately measured density and viscosity data for MEG, DEG, TEG and their mixtures at high temperatures (from 293 K to 465 K) and high pressures (up to 245 MPa).

2. Experimental

2.1. Viscosity measurements

In order to measure dynamic viscosity of pure MEG, DEG, TEG and their binary, (50%MEG + 50%DEG), (50%MEG + 50%TEG), (50%DEG + 50%TEG), and ternary (33.33%MEG + 33.33%DEG + 33.34%TEG) mixtures at temperatures from 293 K to 465 K and at high pressures (up to 245 MPa) the falling-body method (relative version) was used. The experimental details (physical basis and the theory of the method, the apparatus, the procedure of the measurements, and the uncertainty assessment) of the viscosity measurements have been described in detail in our recent publication [1] (see also Refs. [8,9]). Below brief information will be given.

The core of the apparatus is the high pressure measuring cell which consists of tube (viscosimetric or fall-tube). The body is falling coaxially in the fall-tube with the length of 120 mm (the inner diameter is 6.122 mm, and the thickness of the tube wall is 1 mm). The body shape is cylinder with spherical lower end. The optimal height of the body is $h \approx 1.75d$, where d is the diameter of the body. We used various (11) bodies which were made from steel 2X13 with different diameters from 5.605 mm to 6.090 mm. To measure the falling time of the body two transducers were used. One of them was used to measure the viscosity of liquids below 100 mPa s and the other one for measurements of η between 100 and 1500 mPa s.

Viscosity and density measurement systems were located in the high-pressure autoclave. Temperature inside the thermostat was maintained uniform within 0.02 K. Distillated water or silicone (PES-5) was used as a thermostating liquid. Temperature in the upper and lower parts of the autoclave was controlled with copper–constantan thermocouples. Two compensate heaters were used to avoid possible temperature gradient along the autoclave. The regulator provided the maintenance constant temperature in the thermostat within 0.05 K. Uniformity of the temperature distributions along the autoclave was checked with thermocouple probe. The temperature variation during the experiment is less than 0.05 K. All experimental viscosity data presented in this work have been measured several times (3 times) to ensure its reproducibility within 1.0%. The measurement for each data point takes about 300 s around room temperatures and slightly lower at high temperatures. The sample temperature was measured with a platinum resistance thermometer (PRT-10) which resistance ratio is $R_{100}/R_0 = 1.39243 \pm 0.00103$ ($R_0 = 10.0804\ \Omega$). The PRT-10 was calibrated by VNIIFTRI (All Russian Research Institute of Physical Technical Measurements, Moscow, 2011) on ITS-90. Pressure in the system was generated and measured with a dead-weight pressure gauge MP-2500 with an uncertainty of 0.05%. The falling time of the body and monitoring of the core position was performed using the electronic-monitoring system. The body falling can also be monitored on the oscillography screen (СЧ-48Б).

2.2. Working equation for viscosity

The final working equation for viscosity measurement in this method at any experimental T and P conditions is [1,8,9]

$$\eta = \exp\{[-a_0 + \ln W_{pT} + (1 - a_2)\ln \delta_{pT} + a_2 \ln D_{pT} + (1 + a_1)\ln \rho_{pT} + a_1 \ln G_{pT}](1 + 2a_1)^{-1}\}. \quad (1)$$

where the values of parameters a_i ($i = 0, 2$) were determined using the calibration procedure [1,8,9], the definitions of W, δ, D, and G were given in our previous publication [1] (see also below). In order to calibrate the viscometer various liquids (n-hexane [73,74], water [75], IAPWS formulation, International Standard, polymethylsiloxane-5, and polymethylsiloxane-200 [76]) with the well-known viscosities in the range from 0.3184 mPa s to 191.47 mPa s were used. To calibrate the falling body time, viscosity measurements were performed at 293 K and atmospheric pressure with the falling-tube filled with various reference fluids mentioned above. The uncertainties of calibrating liquids viscosity and density at atmospheric pressure and at temperatures from 293 K to 473 K were 0.5% and 0.005%, respectively. The purity of the calibrating liquids was 99.0% and was provided by ЗАО "BIOCHIM" and Novocherkask Syn. Prod. Comps. (Russia). The purities of the calibrating liquids were also additionally checked by measuring the density, viscosity, and refraction index at room temperature (293 K) and at atmospheric pressure. The results are: n-hexane ($\rho = 659.5$ kg m^{-3}, $n_D = 1.3749$, $\eta = 0.3148$ mPa s), polymethylsiloxane-5 ($\rho = 919.3$ kg m^{-3}, $n_D = 1.3988$, $\eta = 5.2974$ mPa s), polymethylsiloxane-200 ($\rho = 971.7$ kg m^{-3}, $n_D = 1.4050$, $\eta = 191.47$ mPa s). We used five different bodies with following characteristic: diameter d of the body from 5.801 mm to 5.989 mm, mass from 1.8626 g to 2.0562 g, and $0.950 \le k \le 0.981$, where $k = d/D$, D is the diameter of measuring tube. Using the calibration procedure [1] the values of parameters $a_0 = -2.8892$, $a_1 = -1.0000$, and $a_2 = 4.0984$ in the relation (1) were determined. Variations of the geometrical size (diameter of the body d and measuring tube D) of the viscometer with temperature T and pressure p were calculated using the elastic theory of materials. The following equations were used to calculate the quantities in Eq. (1)

$$\ln W_{pT} = \ln(l^c_{p_0T_0} \Delta_{3T}) - \ln \tau_{pT}, \quad (2)$$

$$\delta_{pT} = D_{p_0T_0} \Delta_{1T} \Delta_{1p} - d_{p_0T_0} \Delta_{2T} \Delta_{2p}, \quad (3)$$

$$G_{pT} = V^b_{p_0T_0} \Delta_T \Delta_p (\rho_b - \rho_{pT}) g, \quad (4)$$

In Eqs. (2)–(4) $l^c_{p_0T_0}$, $D_{p_0T_0}$, $d_{p_0T_0}$ are the geometric size of the wire (length), measuring tube (diameter), and falling body (diameter) at calibration temperature of $T_0 = 293$ K and pressure of $p_0 = 0.098$ MPa, $V^b_{p_0T_0}$ is the volume of the body at calibrating conditions which were determined by weighing procedure in water and in the air, V^b_{pT}, ρ_b, τ_{pT} are the volume, density, and falling time of the body at experimental (p, T) conditions, respectively. The effect of temperature (Δ_{1T}, Δ_{2T}, Δ_{3T}, Δ_T) and pressure (Δ_{1p}, Δ_{2p}, Δ_p) on the geometrical characteristics of the viscometer supply elements were taken into account using the following relations: