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Tris(2-ethylhexyl) trimellitate (TOTM) as a potential industrial reference fluid for viscosity at high temperatures and high pressures: New viscosity, density and surface tension measurements

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ABSTRACT

Tris(2-ethylhexyl) trimellitate (TOTM) was recently suggested as a reference fluid for industrial use associated with high viscosity at elevated temperature and pressure. Viscosity and density data have already been published on one sample covering the temperature range (303–373) K and at pressures up to about 65 MPa. The viscosity covered a range from about (9 to 460) mPa s. In the present article we study several other characteristics of TOTM that must be available if it were to be adopted as a standard. First, we present values for the viscosity and density obtained with a different sample of TOTM to examine the important feature of consistency among different samples. Vibrating-wire viscosity measurements were performed at pressures from (5 to 100) MPa, along 6 isotherms between (303 and 373) K. Density measurements were carried out from (293 to 373) K up to 68 MPa, along 4 isotherms, using an Anton Paar DMA HP vibrating U-tube densimeter. Secondly, we report a study of the effect of water contamination on the viscosity of TOTM, performed using an Ubbelhode viscometer under atmospheric pressure. Finally, in order to support the use of TOTM as a reference liquid for the calibration of capillary viscometers, values of its surface tension, obtained by the pendant drop method, are provided.

1. Introduction

The International Association for Transport Properties (IATP) has created an internal project regarding the search of a high-viscosity, industrial standard fluid for viscosity for high pressures and high temperatures. One need that is currently being addressed is a high-temperature, high-pressure, deep-water viscosity standard [1] to approximate to the viscosity of crude oil found in very deep off shore wells in the Gulf of Mexico. The IATP has been pursuing such a standard reference liquid for the calibration and validation of viscometers. In the last decade a considerable amount of effort has been devoted to the characterization of diisodecyl phthalate (DIDP) [2–9], and this liquid is currently being used as a standard reference liquid by some authors [8,10]. However, a problem for its future use has been reported [10] because the commercial supplier of high purity DIDP will soon end its production. Comuñas et al. [10,11], Mylona et al. [12] and Harris [3] have therefore suggested squalane could be a substitute, but this liquid has a much lower viscosity than DIDP near room temperature and ambient pressure.

Harris reported high-pressure viscosity measurements on two viscous liquids that may be useful as high-temperature, high-viscosity reference materials [13]. One, is the perfluoropolyether oil, Krytox GPL 102, which is currently the subject of a round-robin comparison of high pressure viscosity measurements on a specific sample by a group of laboratories worldwide under an IUPAC project, employing a variety of viscometric techniques. The viscosity measurements published by Harris [13] have been carried out on Krytox GPL 102 lot K2391. That author reported an average

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deviation of 20% of his results from those obtained by Baled et al. [1] with an unspecified lot of Krytox GPL 102. Fortin [14] has presented results of viscosity measurements of Krytox GPL 102 for two different lots (K1537 and K2391) and indicated a significant difference in the viscosity between the two lots of up to 15%. Bair [15] has also measured the Krytox GPL 102 lot K2391 and compared the viscosity results to those obtained at 40 °C, in a range of pressures, in his laboratory for lot K1537, obtaining a difference greater than 10%, between the two lots. The studies mentioned strongly suggest that the polydispersity of the perfluoropolyether, GPL 102, poses a serious obstacle to its possible use as a standard, given that the viscosity seems to be highly dependent on the lot [15].

Recently, we have proposed tri(2-ethylhexyl) trimellitate (TOTM) as a complement to the earlier proposal of DIDP, aiming at higher viscosities and higher temperatures and pressures, and reported viscosity measurements at pressures up to 65 MPa at six temperatures in the range (303–373) K [16]. The measurements were made by means of the vibrating-wire technique. For comparison a few capillary viscosity measurements were carried out at atmospheric pressure. Complementary density measurements, covering the temperature and pressure ranges of the viscosity measurements were also carried out using an Anton Paar vibrating U-tube density meter [17]. The results were used to construct a hard-spheres correlation scheme for viscosity for this fluid [16]. In the view of the present authors, TOTM has significant potential to be a standard for high viscosity at high temperature and high pressure given the difficulties associated with other materials.

This paper presents new viscosity and density measurements performed on a new lot of TOTM, for comparison with our previous data [16,17]. The evidence of work on other liquids suggest that such a study is important if a material is to be advocated as a standard reference material. The opportunity has been taken to perform other studies that further the adoption of TOTM as a reference material. In particular, we have examined the effect of water on the viscosity of TOTM using a capillary technique and made surface tension measurements by the pendant drop method.

2. Materials and methods

2.1. Materials

The tris(2-ethylhexyl) trimellitate (CAS-No. 3319-31-1 and EC-No. 222-020-0) was acquired from Sigma Aldrich with a nominal minimum purity of 99% and its purity was verified by ^{1}H and ^{13}C nuclear magnetic resonance spectrometry (NMR), and no contamination was detected. The samples were dried with molecular sieves from Sigma Aldrich, with 0.4 nm porosity, and no further purification was performed. Before introduction into the vibrating-wire measurement cells, TOTM was filtered with an inline 15 μm porosity sintered stainless steel filter. The sample was degassed previously to the vibrating wire viscosity measurements. The water content was monitored, before and after all the viscosity and density measurements, using a Karl–Fischer 831 KF Coulometer from Metrohm. We had at our disposal two samples (A and B) of TOTM supplied from the same source with different lot numbers as indicated in Table 1; Sample A was the one used in our earlier work [16,17]. Present density and the vibrating wire viscosity measurements employed sample B. Micro-Ubbelohde capillary was performed in the studies of the effect of water on the viscosity of TOTM, using sample A. Surface tension measurements were made with both samples. Table 1 summarizes the main characteristics of the TOTM samples. The toluene was used to verify the calibration of pendant-drop method used for surface tension measurements.

2.2. Vibrating-wire method and setup

The vibrating wire viscometer was used in the forced mode which requires acquisition of the frequency response of the sensor around the resonance frequency [18]. The experimental procedure to determine the viscosity, in particular, the acquisition of the raw data and the electronic instrumentation used in the present work was previously described by Diogo et al. [19,20]. The vibrating wire sensor used in this work for measuring viscosity at high pressures and at in a wide range of temperatures was recently designed in our group and has been fully described in Ref. [16]. The vibrating wire sensor has a tungsten wire with a nominal diameter of 300 μm. In this work all organic polymeric insulators in the supports of the vibrating wire sensor were replaced by ceramic insulators in order to enable its use at higher temperatures. The setup used for vibrating wire viscosity measurements was fully described previously by Diogo et al. [16]. In this work the pressure measurements above 70 MPa were made with a Heise gauge model CM, with a maximum working pressure of 138 MPa and an uncertainty of ±0.14 MPa.

The expanded uncertainty of the present vibrating-wire measurements, at a 95% confidence level, is estimated to be less than ±2%, for viscosities up to 68 mPa s, less than ±2.6% for viscosities between (69 and 268) mPa s and less than ±3% for higher viscosities. These estimates were partly based on previous sensitivity studies [19–25]. The repeatability of the measurements, at the same confidence level, is better than ±0.2% for the lowest viscosity, increasing to a maximum of ±0.4% for the highest viscosity.

2.3. Capillary viscosity measurements

In order to assess the effect of water impurities upon the viscosity of TOTM independent measurements of the viscosity of tris(2-ethylhexyl) trimellitate at atmospheric pressure were performed using an automatic Schott ViscoSystem® AVS 440 measuring unit fitted with a micro-Ubbelohde viscometer of type 537 23/IIc, manufactured by Schott Instruments GmbH. The experimental setup and procedure were previously described by Diogo et al. [16,26]. Based on previous sensitivity studies [19,23,26] the overall maximum uncertainty of these viscosity measurements was estimated as ±1%. In order to obtain TOTM samples with different water content, a flask with sample A of TOTM was exposed to moist air over several days.

Table 1
Characterization of the liquids used in this work.

Liquid	Sample	Lot number	Source of sample	Water content (mg kg^{-1})	Purity (mass fraction)
TOTM	A	MKBH8084V	Sigma Aldrich	[a]	99%[b]
	B	MKBQ0304V	Sigma Aldrich	[a]	99%[b]
Toluene		–	Sigma Aldrich	–	99.7%

[a] The water content of the samples before viscosity measurements is reported in Table 4.

[b] Nominal mass fraction purity reported by the supplier.