Solar Energy 137 (2016) 385–392

Contents lists available at ScienceDirect

Solar Energy

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

Accurate viscosity measurement of nitrates/nitrites salts for concentrated solar power

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ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form 27 July 2016
Accepted 23 August 2016

Keywords:
Viscosity
Nitrates/nitrites salts
Concentrating solar power
Molten salts

ABSTRACT

Hitec ($NaNO_3$-$NaNO_2$-KNO_3) and Solar salt ($NaNO_3$-KNO_3) are two of molten salts extensively used in Concentrated Solar Power (CSP). Viscosity plays an essential role in process of heat transfer for CSP system. However, it has some certain deviation and unsatisfactory errors among different reports; additionally, it still lacks the data close to melting point, which also makes another barrier for their application. In this work, accurate viscosity data of Hitec and Solar salt with 2.5% uncertainty were systematically measured using an optimized rotational coaxial cylinder in a wide temperature range that fill in the blanks of the existing data. Meanwhile, relevant viscosity were explicitly summarized and particularly analyzed based on the experimental data. Viscosity of the specific components of emerging ternary nitrates ($Ca(NO_3)_2$-$NaNO_3$-KNO_3, $LiNO_3$-$NaNO_3$-KNO_3 and $Ca(NO_3)_2$-$LiNO_3$-KNO_3 mixtures) having potential applications for CSP systems were measured in the high temperature areas for the first time.

1. Introduction

Molten salts have been widely used to be as one of ideal heat transfer and thermal storage media in solar power fields because of large specific heat capacity, low viscosity, wide temperature range and good compatibility to alloys (Yang and Garimella, 2010; Frank et al., 2012; Peng et al., 2010; Chen et al., 2011). Thermo-physical properties of molten salts dramatically impact their heat transfer and thermal storage performances. For example, high boiling and low melting point can improve the efficiency of power generation; large specific heat capacity can reduce the usage amount of molten salt; viscosity can affect the velocity distribution of molten salts fluids and determines their boundary layer thickness, which can influence the efficiency of heat transfer. There was one point to be mentioned, viscosity is also the source of the flow resistance that could increase the energy consumption of pump power (Kearney et al., 2003). Therefore, it is very essential to obtain precise experimental data of thermo-physical properties, especially viscosity, to evaluate heat transfer and thermal storage performance, and to provide significant parameters for the safety design of the solar power systems.

The practical determination of molten salt viscosity is very difficult, due to the obstacles in high-temperature (more than 1000 K) experimental measurement caused by the special features of molten salts, such as low detection limit (lower than 1 mPa s), serious material corrosion and accurate measurement of sample temperature (Nunes et al., 2003). Only few techniques, including capillary method, torsional vibration method, and rotational method, have been proposed. The application of capillary method at high temperature, using both the Ostwald and Ubbelohde design, is dramatically complicated due to the possibility of a change of the capillary diameter caused by corrosion, or by recrystallization of molten salts on the surface of the capillary material (Cohen and Jones, 1957). Furthermore, the oscillating-cup method has extensive application to ionic melts where the viscosities fall into the range 0.5–10 mPa s, and is in general not feasible for systems of viscosities larger than 10 mPa s. For rotational method, especially rotating cylinder technique with a large measuring range (0.1–10^6 mPa s), the high accuracy and reproducibility can be easily achieved because of its definite physical meaning, mathematical simplification, direct and precisely measurement of the sample temperature (Mill, 1995; Cohen and Jones, 1957).

Molten nitrates/nitrites, one kind of heat transfer and thermal storage media, have been extensively employed in concentrating solar power (CSP) systems (Siegel et al., 2011; Serrano-López et al., 2013; Yang and Garimella, 2010; Coscia et al., 2013). Molten nitrates/nitrites based heat transfer fluids (HTFs) are commonly used in modern CSP systems with the first molten salt power tower systems launched in 1984. These pioneering systems were the

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http://dx.doi.org/10.1016/j.solener.2016.08.037
0038-092X/

THEMIS tower in France and Molten salt electric experiment in the United States. As previously described, another important advantage of utilizing nitrates/nitrites salts in the power tower systems is their capability for thermal energy storage. These successful CSP systems include the Eurelios power project in the Italy and the Solar Two project in the United States (Dunn et al., 2012; Vignarooban et al., 2015).

So far, Hitec ($NaNO_3$-$NaNO_2$-KNO_3, 7–40–53 wt.%) and Solar Salt ($NaNO_3$-KNO_3, 60–40 wt.%), have been successfully applied in CSP (Boerema et al., 2012; Singh, 1985; Yang and Garimella, 2010). In addition, in order to improve the heat transfer and thermal storage performance and reduce the system cost, some emerging ternary nitrates ($Ca(NO_3)_2$-$NaNO_3$-KNO_3, $LiNO_3$-$NaNO_3$-KNO_3 and $Ca(NO_3)_2$-$LiNO_3$-KNO_3 mixtures) which have great potential applications for CSP systems were prepared (Bradshaw, 2010). Based on the usage as working fluid in CSP, these molten salts have received attention, especially the viscosity playing an important role in calculations or simulations for thermal exchange and storage system design. For Hitec, initial measurements of the viscosity was performed by Kirst et al. (1940) using an Ostwald viscometer, and then by Gaune (1982) and Chen et al. (2011) using an oscillating right-circular cylinder viscometer and oscillation cup viscometer respectively. In addition, the data have been also reported in the open literatures (Geiringer, 1962; Singh, 1985; Coastal Chemical Co., 2011; McDuffie et al., 1963; Yang and Garimella, 2010; Bohlmann, 1972). Molten $NaNO_3$-KNO_3 with a eutectic point at 45.7 wt.%, $NaNO_3$ and 54.3 wt.% KNO_3 (mol composition: $NaNO_3$-KNO_3, 50–50 mol.%) has been extensively studied, whereas, the commercial Solar salt with a composition ($NaNO_3$-KNO_3, 60–40 wt.%) has sparse data reported, because the viscosities of the two compositions were supposed to be basically the same (Serrano-Lopez et al., 2013). Viscosity of the equimolar mixture $NaNO_3$-KNO_3 has been measured by Murgulescu and Zuca (1969) utilizing an improved damped oscillating sphere method and by Coscia et al. (2012) with a Rheometric ARES Rheometer using a fixed Couette, and the data of viscosity from Mar et al. (1982) and Nissen (1982) were also presented. Different compositions of the emerging ternary nitrates system have been investigated because different phase diagrams have been published in the open literature (Menzies and Dutt, 1911; Jänecke, 1942; Levin et al., 1956; Gomez et al., 2013), however, few sporadic viscosity data have been obtained (Menzies and Dutt, 1911; Jänecke, 1942; Bergman et al., 1955; Levin et al., 1956; Kearney et al., 2003; Brosseau et al., 2004; Bradshaw, 2010; St. Laurent et al., 2000; Siegel et al., 2011).

The viscosity data of these molten nitrates/nitrites mixtures used for CSP systems are still insufficient although they have been studied by many researchers with experimental measurements and calculations. Firstly, viscosity data of molten nitrates/nitrites have particularly large deviation among different researchers reported in open literatures in that the low viscosity measurement of molten nitrates/nitrites are difficult under high temperature. For example, for Hitec, the maximum deviation was more than 50% (at 700 K). Moreover, the measurement errors were wrongly defined or not referred in some experimental data. Secondly, the viscosity data of these molten nitrates/nitrites mixtures are seriously insufficient. Many viscosity data are lacking under condition close to melting point, which can provide significant parameters for the safety analysis of molten salt thermo-hydraulic loop under abnormal working conditions. In addition, viscosity data of the emerging ternary nitrates, especially the components in this work, are still nonexistent at high temperature.

In present paper, accurate viscosity measurements of the molten nitrates/nitrites were systematically conducted using an optimized rotational coaxial cylinder in a wide temperature range. The viscosity data of extensively used molten Hitec and Solar salt were detailed summarized and reassessed based on the experimental data. The viscosity of the emerging ternary nitrates was systematically analyzed. The reliability and accuracy of these viscosity data were analyzed and evaluated. These reliable viscosity results fill in the blanks of the existing data, which is beneficial to the design of CSP systems.

2. Experimental procedure

2.1. Sample preparation

Table 1 shows the components of binary and ternary nitrates/nitrites molten salts for measurements in this paper. The molten salt mixtures were prepared from $NaNO_3$, $NaNO_2$, KNO_3, $LiNO_3$ and $Ca(NO_3)_2$-$4H_2O$ salts (Analytical reagent). These salts were separately dried at 400 K under argon atmosphere for 24 h, and then mixed in graphite crucibles. The mixed nitrates/nitrites were heated to 500 K, and keep this temperature for 24 h in the argon atmosphere. For calcium nitrate containing salts, other than the separately dried, the salts were heated to 620 K under argon atmosphere for 24 h to allow the water of hydration of the calcium nitrate constituent to evolve slowly.

2.2. Measurement apparatus

The viscometer used in this work is based on coaxial cylinder method, shown in Fig. 1. The viscometer mainly consists of four fundamental systems: the measuring unit, the spindle and crucible, a high temperature furnace, and other auxiliary system.

This measuring unit is improved on the basis of Brookfield DV-III. With an aim to guarantee the turbulence nonexistence in the sample liquids during measurement process, suitable rotational speed and the sizes of spindle and crucible were selected through calculations and pre-experiments. The crucible with inner diameter of 29 mm and the depth of 220 mm, and the spindle with diameter of 26 mm and length of 150 mm were made of graphite. Under such conditions, the measurement range was 1.6–16 mPa s in a speed of 30 Revolutions Per Minute (RPM). In order to get the exact temperature of molten sample, a K-type thermocouple was put into the sample fluid.

For rotating cylinder viscometer, the viscosity is obtained by formula (2) derived from formula (1) which is deduced by using $SMC = \left(\frac{1}{r^2} - \frac{1}{R^2}\right) \Big/ 120(h + c)$. The standard sample with viscosity

Table 1
Compositions and melting point of the binary and ternary nitrates/nitrites mixtures system in this work.

Composition	$LiNO_3$ (wt.%)	$NaNO_3$ (wt.%)	$NaNO_2$ (wt.%)	KNO_3 (wt.%)	$Ca(NO_3)_2$ (wt.%)	Melting point (K)
Hitec		7	40	53		415
Commercial solar salt		60		40		511
Equimolar $NaNO_3$-KNO_3		45.7		54.3		495
$LiNO_3$-$NaNO_3$-KNO_3	23.4	17.3		59.3		413
$Ca(NO_3)_2$-$NaNO_3$-KNO_3 [a]		16		48	36	406
$Ca(NO_3)_2$-$LiNO_3$-KNO_3	21.7			58.3	20	390