Viscosity analysis of alkali metal carbonate molten salts at high temperature

Sun Woog KIM, Kazuyoshi UEMATSU,* Kenji TODA† and Mineo SATO‡

Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950–2181, Japan
*Department of Chemistry and Chemical Engineering, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950–2181, Japan

The viscosities of unary, binary, and ternary eutectic alkali metal carbonate molten salts were measured for the first time by a rotation method using a high-temperature rheometer system and the reliability of the viscosity values was evaluated. The viscosity values obtained in this study are similar to that reported by Sato’s research group, which is considered to have the highest reliability among the studies reported till date. The standard errors in the viscosity values at each temperature are less than ±5%.

©2015 The Ceramic Society of Japan. All rights reserved.

Key-words : Viscosity analysis, Alkali metal carbonate molten salts, Rotation method

1. Introduction

Solar energy, including light and thermal, has attracted considerable attention as a renewable energy alternative to fossil fuels. Thermal energy storage (TES) techniques are currently considered effective methods for using solar energy without time-dependent limitations.1–3) In particular, concentrating solar power (CSP) plants employing TES techniques can generate electricity even if sunlight is not available and the successful operation of these plants has been demonstrated at both experimental and commercial scales.8,9) In solar thermal energy systems, TES is based on either sensible heat storage (SHS) or latent heat storage (LHS) using a phase change material or thermo-chemical storage.5,6) Among these, LHS has been suggested as the most effective method in solar thermal energy applications because it exhibits small temperature fluctuations during heat storage and retrieval processes.6,10,11)

Among several phase change materials, alkali metal molten salts are the most promising candidates for use as thermal storage media and heat transfer fluids in solar thermal energy systems. In particular, at high temperature, these materials can improve the energy conversion efficiency and reduce the cost of electricity production.12,13) It is well known that alkali metal molten salts remain as stable solids at room temperature and transform to the liquid phase at elevated temperatures. In addition, alkali metal molten salts have a number of advantages, such as a low melting point, high heat capacity, moderate energy density, and a high boiling point.14) Moreover, molten salts are less expensive and more environmentally friendly than currently available high-temperature oils. Therefore, many investigations have been devoted to searching for novel molten salts to enhance the energy storage efficiency of solar thermal energy system.13–16) However, there are scarce investigations focusing on thermo-physical properties, especially viscosity, of molten salts at high temperature. Determination of molten salt viscosity is significantly important for application of the molten salt as a heat transfer fluid in solar thermal energy systems to ensure that the molten salt can be transported from a solar field to a thermal storage system with minimal thermal energy loss. Several methods have been reported for analyzing the viscosities of molten salts, including rotation, oscillation, and capillary methods. Oscillation is most frequently used in the analysis of molten salt viscosity at temperatures above 773 K.17–19) However, since most oscillating crucible or pendulum viscometers are custom instruments, the viscosity values of molten salts obtained by oscillation have large variability. In addition, the oscillation method requires long analysis times, approximately 48 h, to obtain an accurate measurement of molten salt viscosity.20,21) The oscillation method also requires accurate information about the molten salt density, indicating that this method is unsuitable for measuring the viscosity of complicated mixed molten salts above quaternary eutectic system.

In this study, a rotation method was used to measure viscosity of molten salts because the viscosity can be acquired in a short measurement time, and the density of the molten salt is not required. To date, there have been no reports on the viscosity of molten salts determined using the rotation method at temperatures above 773 K, because it is difficult to measure low viscosities at high temperatures with this method. In a typical rotational viscometer, thermal radiation from the heating system influences the rotation of the cylinder motor. The rotational speed of the cylinder is difficult to measure at high temperature, leading to larger errors in the measured viscosity values. In addition, these viscometers have low sensitivity, making the measurement of low viscosities even more challenging.

The viscosities of unary, binary, and ternary eutectic alkali metal carbonate molten salts were successfully measured in this work by a rotation method using a high-temperature rheometer system equipped with a special heating unit. Viscosity values were confirmed to have high reliability by comparing to previously reported results.20,21)

2. Experimental

2.1 Preparation of carbonate molten salts

Na2CO3 (Kanto Chemical, Co., Inc., 99.8%), Li2CO3 (Kanto Chemical, Co., Inc., 99.8%), and K2CO3 (Kanto Chemical, Co.,
Inc., 99.8%) were used as starting materials in the preparation of carbonate molten salts. Each alkali metal carbonate molten salt was prepared by heating for 1 h at a temperature above each salt’s melting temperature, followed by cooling room temperature rapidly. Li₂CO₃ was heated at 1073 K, and binary and ternary eutectic carbonate molten salts, xLi₂CO₃−(1−x)K₂CO₃ (0.30 ≤ x ≤ 0.60) and 0.250Li₂CO₃−0.435Na₂CO₃−0.315K₂CO₃, were heated at 873 K for 1 h.

2.2 Viscosity analysis
The thermostat and the viscometer cylinder were heated to 1073 K for the unary Li₂CO₃ and binary eutectic xLi₂CO₃−1−xK₂CO₃ (x = 0.30) molten salts and to 873 K for the binary eutectic xLi₂CO₃−1−xK₂CO₃ (0.46 ≤ x ≤ 0.60) and ternary eutectic 0.250Li₂CO₃−0.435Na₂CO₃−0.315K₂CO₃ molten salts to uniformly melt each sample. The viscosities of Li₂CO₃, xLi₂CO₃−1−xK₂CO₃ (0.30 ≤ x ≤ 0.60) and 0.250Li₂CO₃−0.435Na₂CO₃−0.315K₂CO₃ molten salts were measured at temperatures above the melting temperature and below the boiling temperature of the respective molten salts by the rotation method using high-temperature rheometer system (MCR 502, Anton paar). The viscosity measurements were performed 36 times for 6 min at each temperature.

2.3 Viscometer
Figure 1 shows a photograph of the high-temperature rheometer system, which comprises a high-temperature rotational viscometer equipped with a special heating unit for measuring the viscosities of molten salts at temperatures over 773 K. The interior of the special heating unit is maintained at a uniform temperature during viscosity measurements by circulation of a gas, such as air, N₂, or Ar. The high-temperature rheometer system has a cooling system so that the cylinder motor is nearly impervious to the heating temperature inside the unit. Furthermore, the viscosity measurement times at each temperature are short.

3. Results and discussion
Figure 2 shows the temperature dependence of the viscosity of unary Li₂CO₃ molten salt. The conventional viscosity data of Li₂CO₃ reported by Janz’s and Sato’s research groups measured by the oscillation method are also plotted in Fig. 2 for comparison.

Because the melting and boiling temperatures of Li₂CO₃ molten salt are 996 and 1383 K, respectively, the viscosity of Li₂CO₃ molten salt was measured over a temperature range from 1003 to 1173 K and the standard error was found to be ±5%. The viscosity of Li₂CO₃ molten salt monotonically decreases with increasing temperature consistent with other reports of molten carbonate salts.20–22 The viscosity of Li₂CO₃ molten salt measured at 1023 K is 7.1 mPa s. Although these results are slightly different than those reported by Janz’s research group, they are similar to results reported by Sato’s group. Sato measured the viscosities of alkali metal carbonate and halide molten salts using oscillation and capillary methods. Consequently, the viscosity values measured by Sato’s are considered to have the highest reliability among the studies reported till date. Our viscosity results have high reliability at high temperature.

Figure 3 shows the temperature dependence of the viscosity of binary eutectic 0.46Li₂CO₃−0.54K₂CO₃ molten salt. The viscosity data of the molten salt reported by Sato’s research group are also plotted as a reference. Over a temperature range from 773 to 1123 K, the viscosity difference at each temperature are within approximately ±5%. The binary eutectic 0.46Li₂CO₃−0.54K₂CO₃ molten salt measured in this study shows linear Arrhenius behavior over the wide measurement temperature range. The viscosity at 923 K was 8.2 mPa s, which is similar to the viscosity measured by Sato. In addition, the binary eutectic xLi₂CO₃−(1−x)K₂CO₃ (0.30 ≤ x ≤ 0.60) molten salts also show viscosity behavior similar to that of the 0.46Li₂CO₃−0.54K₂CO₃ molten salt. The viscosities of all xLi₂CO₃−(1−x)K₂CO₃ (0.30 ≤ x ≤ 0.60) molten salts gradually decrease linearly with increasing temperature. These results indicate that the xLi₂CO₃−(1−x)K₂CO₃ (0.30 ≤ x ≤ 0.60) molten salts are the molten state over the entire
temperature range, and the obtained viscosity data are highly reliable at high temperature.

**Figure 4** shows the isothermal viscosities for binary eutectic 
\[ x \text{Li}_2\text{CO}_3 \cdot (1-x)\text{K}_2\text{CO}_3 \] molten salts. The broken line represents the viscosity at the liquidus temperature for each composition, which was calculated from the phase diagrams and the equation, log \( \eta = ( -0.9506 - 0.5205X_K + 0.7388X_K^2 ) + (1820 - 9.04X_K - 402.2X_K^2)/T \), where \( \eta \) is the viscosity of binary eutectic 
\[ x \text{Li}_2\text{CO}_3 \cdot (1-x)\text{K}_2\text{CO}_3 \] molten salts, and \( X_K \) is the molar fraction of \( \text{K}_2\text{CO}_3 \) salt.\(^{20,21}\) The isothermal viscosities of binary eutectic 
\[ x \text{Li}_2\text{CO}_3 \cdot (1-x)\text{K}_2\text{CO}_3 \] molten salts clearly show downward convex curves at all temperatures. The viscosities of binary eutectic 
\[ x \text{Li}_2\text{CO}_3 \cdot (1-x)\text{K}_2\text{CO}_3 \] molten salts show a clear dependence on the melting temperature of each composition.

**Figure 5** shows the temperature dependence of the viscosity of ternary eutectic \( 0.250\text{Li}_2\text{CO}_3 \cdot 0.435\text{Na}_2\text{CO}_3 \cdot 0.315\text{K}_2\text{CO}_3 \) molten salt. This is the lowest-melting temperature composition (m.p. 668 K) of this ternary alkali metal carbonate salt. The viscosity of the ternary eutectic molten salt was measured over a temperature range from 693 to 1023 K and the standard error at each temperature is within approximately ±5%. In addition, decomposition of the ternary eutectic carbonate molten salt was not confirmed at 1023 K. The viscosity of \( 0.250\text{Li}_2\text{CO}_3 \cdot 0.435\text{Na}_2\text{CO}_3 \cdot 0.315\text{K}_2\text{CO}_3 \) linearly decreases with increasing temperature. The obtained viscosity behavior of the ternary eutectic \( 0.250\text{Li}_2\text{CO}_3 \cdot 0.435\text{Na}_2\text{CO}_3 \cdot 0.315\text{K}_2\text{CO}_3 \) molten salt is similar to those of the unary and binary alkali metal carbonate molten salts and the viscosity of the ternary eutectic carbonate molten salt was 7.9 mPa·s at 923 K.

The viscosities of the unary, binary, and ternary eutectic alkali metal carbonate molten salts are accurately measured in less than 3 h despite the wide measurement temperature range (from 693 to 1123 K in the case of ternary eutectic \( 0.250\text{Li}_2\text{CO}_3 \cdot 0.435\text{Na}_2\text{CO}_3 \cdot 0.315\text{K}_2\text{CO}_3 \) molten salt). The measurement time includes heating time for the thermostat and cylinder. This study suggests that the rotation method using a high-temperature rheometer system is suitable for measuring the viscosity of molten salts at high temperatures. This method is expected to find applications in developing novel molten salts for use in solar thermal energy systems as heat transfer fluids.

**4. Conclusion**

The viscosities of alkali metal carbonate molten salts were measured for the first time by the rotation method using a high-temperature rheometer system equipped with a special heating unit. The viscosities of all alkali metal molten salts show linear Arrhenius behavior over the wide measurement temperature range, and the viscosities monotonically decrease with increasing temperature. The viscosities and behaviors of alkali metal carbonate molten salts obtained in this study are similar to those reported by Sato, which are considered to be highly reliable. Viscosities of alkali metal carbonate molten salts can be measured at high temperatures (>773 K) by the rotation method with very low error (<5%).

**Acknowledgements**

This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “energy carrier” (Funding agency: JST).

**References**