

Viscosity of the Eutectic $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ Melt

Tatsuhiko Ejima, Yuzuru Sato, Tsutomu Yamamura, Kyoko Tamal, and Maysayuki Hasebe

Department of Metallurgy, Faculty of Engineering, Tohoku University, Sendai 980, Japan

Mark S. Bohn

Solar Energy Research Institute, Golden, Colorado 80401

George J. Janz*

Rensselaer Polytechnic Institute, Molten Salts Data Center, Department of Chemistry, Troy, New York 12181

The viscosity of the molten eutectic mixture of $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (reagent grade) has been measured to 900 °C by means of the oscillating crucible technique used for measurements in the absolute mode. The viscosity can be expressed by η (mPa·s) = 0.1012 $\exp(33400/RT)$, where R equals 8.3143 J K⁻¹ mol⁻¹, and the accuracy limits are better than ±3%. The present results differ markedly from previously published results, and model calculations show that the differences can be understood, in large part, if the presence of a "voids" effect had escaped detection in the earlier work. Results are also reported for a series of measurements with a commercial grade carbonate eutectic mixture.

The molten ternary carbonate eutectic ($\text{Li}_2\text{CO}_3\text{:Na}_2\text{CO}_3\text{:K}_2\text{CO}_3$ mol %: 43.5:31.5:25.0; mp 397 °C) is of interest as a candidate heat-transfer medium in solar energy storage applications (1-3). The present work was aimed at obtaining reliable viscosity data for this fluid. Previous measurements appear limited to the studies of Janz and Saegusa (4). Doubts on the reliability of these results have emerged in the recent heat transfer/heat calculations by Bohn (5), and, quite independently and almost concurrently, from results reported for molten Na_2CO_3 by Ejima et al. (6, 7). In the former (5), it was found necessary to assume viscosities for the carbonate eutectic approximately 3.5 times larger in order to bring modelling calculations into agreement with the observed thickness of the flowing salt film. In the latter (6, 7), the results for molten Na_2CO_3 differed significantly from the values reported earlier; at 950 °C for example, the viscosity was found to be about 2 times greater than reported earlier (4) for this molten carbonate.

The present communication reports a reinvestigation of the viscosity of the ternary carbonate eutectic using the damped oscillational technique and working equations for calculating the viscosities on an absolute basis. The investigation was extended to include a comparable series of measurements for the eutectic made from commercial grade quality carbonates, and these results are also reported.

Experimental Section

Materials. Both reagent grade (Baker Chemicals) and commercial grade carbonates were used for the preparation of the eutectic mixtures by direct weighings. The overall purity of the commercial grade eutectic was about 98.4% (based on carbonate content). The samples were prepared in kilogram amounts and melted to achieve composition homogeneity. Prior to measurements, aliquots of these samples were dried under vacuum at 300 °C; all further transfers were with the samples under CO_2 atmospheres at pressures sufficient to repress decomposition (to CO_2 and alkali metal oxides). For pretreatment of samples in the viscometer, see later.

High-Temperature Viscometer. All measurements were made with the specially designed high-temperature damped oscillational viscometer at Tohoku University (6, 7); this unit is used in a computer-coupled mode for data acquisition and data reduction to the viscosity values. Details are available elsewhere (8), and it is sufficient to note that the method is used on an absolute basis (i.e., the value of each term in the working equation for the viscosity calculations is determined independently from precise knowledge of the design dimensions of the component parts of the unit, and the fundamental measurement principles). It should also be noted that the Kestin alloy (8% tungsten-92% Pt) was used for the torsion wire; this composition has been highly recommended (9-11) because it has low internal friction and a stable constant of elasticity, and is easily annealed stress-free. The overall accuracy limits for the measurements were estimated to be better than ±3%. A limited series of measurements with molten NaCl confirmed the high-temperature performance to be within 2.5% of the recommendations advanced from the Molten Salts Standards Program (11).

Measurements with Molten Carbonate Eutectic. A series of "performance problems" were encountered which appeared quite unique to work with molten carbonates. The resolution of these were important steps to meaningful results.

i. Apparent Failure of the log (viscosity) vs. T^{-1} (K) Criterion. The oscillational viscometer facility (Tohoku University) is appropriate for measurements of viscosities of 10 mPa·s or less, i.e., the range in which most of the molten salt viscosities are found. The temperature-viscosity correlation for such systems is found to be an exponential function

$$\text{viscosity} = A \exp(E/RT) \quad (1)$$

and it follows from the logarithmic form of eq 1 that log (viscosity) vs. T^{-1} (K) is a straight line function with a slope of (E/R) .

In the earlier stages of the present measurements, an apparent failure of this criterion was observed. The correlation held well for measurements above 700 °C but appeared to "fail" for the results below 700 °C. At 700 °C a sharp inflection occurred with a slope reversal.

This apparent failure was resolved from a consideration of the dimensions as a possible physical limitation of the viscometer. If viscosities of the carbonate eutectic at ~700 °C were exceeding the "10 mPa·s limit", the failure would be due to this rather than due to the onset of an anomalous melt behavior. By modifying the dimensions of the oscillating crucible it was found that the "failure point" was indeed dimensions-dependent. Thus when the cylindrical dimensions were increased from [20 mm (i.d.) × 88 mm] to [25 mm (i.d.) × 100 mm] the measurements could be extended down to as low as ~600 °C. The latter dimensions [25 × 100] were the maximum size that could be used in this assembly without major redesign of the

cylindrical "hot zone" of the viscometer. For the viscosities reported herewith, this larger crucible was used throughout the measurements.

ii. "Melt-Creep" effect. A "melt-creep" effect was yet another problem encountered in the work with these melts. It was first apparent in the work with the commercial grade eutectic where, apparently, the viscosity did not remain constant (at any fixed temperature) but changed as time went on. Inspection after the run showed that the outer surfaces of the crucible had been "wetted" (i.e., some of the molten carbonate had "crept" from the interior and was hanging as a small pendant drop on the crucible bottom).

The melt-creep effect could not be eliminated completely; however, the following procedures were found effective in minimizing this effect.

a. *Pretreatment of the Carbonate Eutectic.* Both the reagent grade and the commercial grade eutectics were pretreated, prior to measurements, by drying under vacuum to the melting point (397 °C) and then by bubbling CO₂ through the melt for ~12 h at 700 °C.

b. *Gold Plating.* Examination of the published results (12–15) for contact angles indicated that the wetting should be minimal for molten carbonates on gold surfaces. The cylindrical nickel crucible was gold-plated both to enhance resistivity to corrosive attack and to decrease melt-creep effects.

c. "Venting". The molten carbonate is normally confined in the cylindrical crucible by a tight fitting (threaded) cap that virtually forms an hermetic seal. It was observed, in a series of tests, that the main wetting or melt-creep effect occurred in the initial stages of the measurements (almost as if there was a degassing effect leading to a forced "gushing" from the confined volume). By drilling two small holes in the crucible cap, to serve as vents, it was found that the melt-creep or gushing phenomenon could be very effectively minimized. The vented-cap modification was thus used throughout the measurements for the results reported in this work.

The overall "weight loss" from the crucible contents was thus minimized to ~0.3% or less. Corrections for this loss (corresponding to a reduced liquid level) were taken into account in the final calculations of viscosities.

iii. "Gas Bubble or Voids" Effect. The "gas bubble or voids" effect can be attributed to a degassing of the molten carbonate (possibly as CO₂) and the adherence of the gases on the interior crucible walls (as firmly adsorbed gaseous films or voids). This would lead to measured values for the viscosity that would be smaller than the true viscosities (since a radius larger than the actual radius of the melt is being "input" into the working equations). When measurements were attempted with the commercial grade eutectic without the CO₂-bubbling pretreatment, the problems from this error source were most pronounced, whereas after the CO₂ pretreatment (bubbling), meaningful measurements were possible.

iv. *Summary.* With due attention to the preceding problem areas, the viscosities of the two samples, reagent grade and commercial grade carbonate eutectic, were measured to ~900 °C as the upper temperature limit. The need for due cognizance of meniscus corrections for viscosity measurements with melts in flat bottom cylindrical crucibles has been considered in some detail by Brockner, Tørklep, and Øye (16). Under the conditions used in the present work (gold plated inner crucible surfaces, with liquid levels approximately, 70% of the crucible depth) the errors due to this possible source appear to be less than 2%, i.e., within the overall accuracy limits of the measurements. Quantitative corrections for this effect accordingly were not attempted.

The additional question of a possible composition change of the samples due to evaporation losses and/or decomposition processes occurring in the course of the measurements was

Table I. Measured Viscosities: Molten Carbonate Eutectic

<i>T</i> , K	viscosity, mPa·s	<i>T</i> , K	viscosity, mPa·s
(a) Reagent Grade Eutectic			
922.6	8.058	1122.1	3.635
972.2	6.326	1172.1	3.148
1021.9	5.090	970.9	6.184
1071.5	4.290		
(b) Commercial Grade Eutectic			
891.5	9.036	1023.2	5.040
922.0	7.862	1073.5	4.219
972.3	6.216	1124.5	3.577
973.4	6.104	1175.1	3.094

also addressed in the present work. The vapor pressure of most ionic molten salt systems is so low that losses due to normal evaporation would not contribute significantly to composition changes. With alkali metal carbonates, losses due to evolution of CO₂ (with concomitant formation of the oxides in the molten liquid salt sample) could induce composition changes. It should be noted here that during the measurements the gaseous atmosphere in the "working zone" was helium with ~50 Torr of CO₂ partial pressure. This CO₂ pressure is larger than the equilibrium CO₂ dissociation pressures (for molten carbonates; 500–900 °C) and yet less than the pressures that introduce instability to the damped oscillation of the crucible (i.e., ~70 Torr). Under these conditions (i.e., ambient CO₂ pressures > thermodynamic CO₂ dissociation pressures) the melt composition is, effectively, held invariant, and corrections for changes in melt composition may be assumed to be negligible.

Results and Discussion

Table I lists the experimental data sets for the reagent grade and commercial grade carbonate eutectics, respectively. Each value is the average of 4–6 measurements. The temperature ranges are those for which the linearity of the log (viscosity) vs. T^{-1} (K) criterion holds. The viscosity–temperature correlations from these data sets are as follows:

(a) reagent grade eutectic

$$\text{viscosity (mPa}\cdot\text{s)} = 0.1012 \exp(33400/RT) \quad (2)$$

(b) commercial grade eutectic

$$\text{viscosity (mPa}\cdot\text{s)} = 0.1039 \exp(33080/RT) \quad (3)$$

where the well-defined linearity of the log (viscosity) vs. T^{-1} criterion in the measurement range justifies the extrapolation to 770 K as the lower limit, and R equals 8.3143 J K⁻¹ mol⁻¹. Based on the combined data sets (Table I), one obtains (c) reagent grade and commercial grade carbonate eutectic

$$\text{viscosity (mPa}\cdot\text{s)} = 0.1038 \exp(33140/RT) \quad (4)$$

which expressed the results for either sample to better than ~1% (i.e., well within the overall accuracy limits of the measurements method, i.e., ±3%).

As noted earlier in this communication, both the reagent grade and the commercial grade eutectics were pretreated prior to the viscosity measurements by drying under vacuum at the melting point (397 °C) and then by bubbling CO₂ through the melt for ~12 at 700 °C. The close correspondence in the results for the two samples is thus for measurements with samples that have been CO₂-equilibrated.

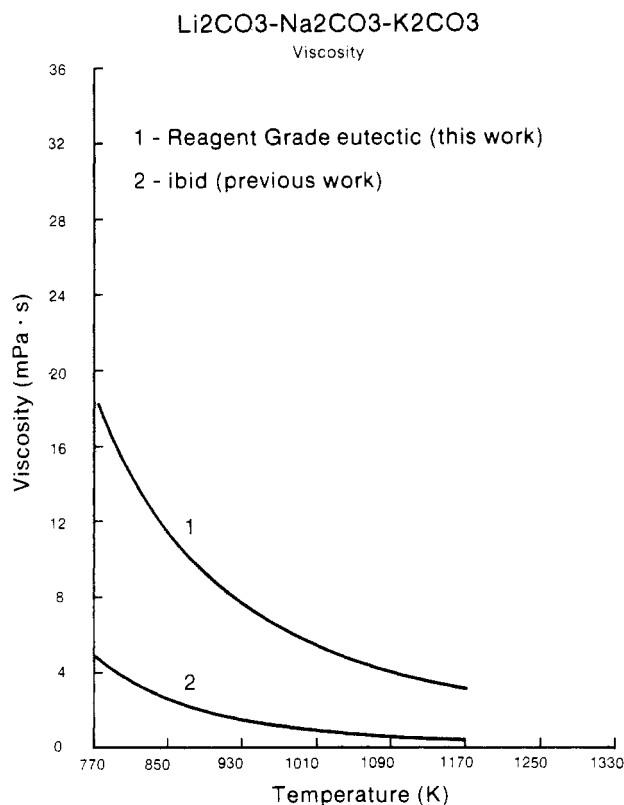
Previous measurements for the reagent grade carbonate eutectic, as already noted elsewhere, are limited to those reported by Janz and Saegusa (4) and were expressed by

$$\text{viscosity (mPa}\cdot\text{s)} = 0.00463 \exp(44600/RT) \quad (5)$$

In Table II and Figure 1, these are compared numerically and graphically. The confidence level in the present work is

Table II. Comparison of Viscosity Results for the Reagent Grade Ternary Carbonate Eutectic with Previously Published Results

temp, K	viscosity, mPa·s		departure, %
	present work	prev work [ref 4]	
770	18.66	4.91	-74
970	6.36	1.17	-82
1170	3.14	0.45	-86

**Figure 1.** Comparison with previously published results.

high; the problem, therefore, is to understand the factors in the earlier work that led to such markedly lower values.

A critical examination suggests two points for which quantitative estimates are possible. In the earlier investigations the density data for the eutectic were calculated from single salts data and theoretical principles. Comparison with the measured results (17) indicates that the error due to this source (estimated densities) leads to values about 10% lower than the correct viscosities. The second point touches on one aspect of the performance problems that had been resolved in the present work, namely the gas bubble or voids effect (see Experimental Section). Using the dimensions of the present crucible and the logarithmic damping as modelling parameters (Tohoku viscometer), it is found (18) that, for an effective melt radius decrease of ~20%, the calculated viscosities would be about ~65%

lower than the true (correct) values.

It is clear from the results of the present measurements, and the preceding considerations, that the earlier work is incorrect. The very low values can be attributed, in large part, to the formation of a firmly adsorbed gaseous film on the inner crucible surfaces, i.e., a voids effect, and that this had escaped detection. Additional factors as possible error sources can be listed, but the impact of these cannot be estimated quantitatively. Further discussion would only be speculative and is deferred accordingly.

Acknowledgment

The task of the measurements was undertaken at Tohoku University through arrangements with the MSDC-RPI. Dr. T. Yamamura held a visiting appointment at RPI for some two months during the period of this work to assist with the data analysis and the almost daily communications with Dr. Y. Sato at Tohoku who carried the responsibilities for the measurements at that center.

Literature Cited

- (1) Coyle, R. T.; Copeland, R. J.; Burrows, R. W.; Gaggin, R. M. *High Temperature Molten Salts for Use in Solar Thermal Energy Systems*; SERI/TR-255-2001; UC 62d; DE 83011997; Dec 1983; NTIS-U.S. Department of Commerce: Springfield, VA 22161.
- (2) Bohn, M. S.; Green, H. J.; Yeagle, G.; Siebarth, J.; Asbell, O. D.; Brown, C. T. *Direct Absorption Receiver Experiments and Concept Feasibility*; SERI/TR-252-2884, Oct 1986; NTIS-U.S. Department of Commerce: Springfield, VA 22161.
- (3) Bohn, M. S. *J. Sol. Energy Eng.* **1985**, *107*, 208.
- (4) Janz, G. J.; Saegusa, F. *J. Electrochem. Soc.* **1963**, *110*(5), 452.
- (5) Bohn, M. S. Solar Energy Research Institute, Golden, Co., private communication to MSDC-RPI, May 1985.
- (6) Ejima, T.; Sato, Y.; Yaegashi, S.; Kijima, T. *Proceedings of the 17th Molten Salts Chemistry Symposium*; The Molten Salt Committee of The Electrochemical Society of Japan: Kobe 657, Japan, 1964; Vol. 17, p 29.
- (7) Ejima, T.; Sato, Y.; Yamamura, T. Tohoku University, Sendai, Japan; prepublication results communicated to MSDC-RPI, May 1985.
- (8) Janz, G. J. *Viscosity Measurement of Molten Carbonate Salt*; SERI/STR-252-2905, Dec 1985; NTIS-US Department of Commerce: Springfield, VA 22161.
- (9) Kestin, J. R.; Mosynski, J. M. Brown University Report AF891/11 (July 1958); AFOSR-7N-58-752, ASTIA Doc. No. 201,576.
- (10) Marvin, R. S. *J. Res. Natl. Bur. Stand.* **1971**, *75A*, 535.
- (11) Janz, G. J. *J. Phys. Chem. Ref. Data* **1960**, *9*, 791.
- (12) Bohn, M. S. Solar Energy Research Institute, Golden, Co., private communication to MSDC-RPI, August 1985.
- (13) Eberhart, J. G. *Abstracts: Interfacial Thermodynamics*; 71st AIChE Meeting, Miami Beach, FL, Nov 1978; The American Institute of Chemical Engineers: New York 10017.
- (14) Moiseev, G. K.; Stepanov, G. K. *Trudy 8-66, Electrochemistry of Solid and Molten Electrolytes 1967*, *5*, 101. English edition: Consultants Bur.; New York.
- (15) Selman, J. R.; Maru, H. C. *Advances in Molten Salts Chemistry*; Mamantov, G., Ed.; Marcel Dekker: New York, 1981; Vol. 5, Chapter 4.
- (16) Brockner, W.; Tørklep, K.; Øye, H. A. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1.
- (17) Ward, A. T.; Janz, G. J. *Electrochim. Acta* **1965**, *10*, 849.
- (18) Sato, Y., unpublished work; private communication to MSDC-RPI, Dec 1985.

Received for review March 17, 1986. Accepted December 2, 1986. This work was made possible, in large part, by a subcontract at RPI from the Solar Energy Research Institute, Golden, Colorado under the program supported under Contract DE-AC02-83CHI10093 at that site.