Viscosity Measurements: Molten Ternary Carbonate Eutectic.

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ABSTRACT

Modelling calculations of falling molten salt films in direct absorption solar energy receivers led directly to questions concerning the reliability of the viscosity data for the ternary carbonate eutectic. The present work was undertaken to resolve this dilemma. A number of performance problems were encountered. The resolution of these and the results for viscosity measurements to 900°C for this molten carbonate system are reported. The results differ markedly from the earlier work, and possible reasons for this are examined.

INTRODUCTION

The molten ternary carbonate eutectic is of interest as a candidate heat transfer medium in solar energy storage applications (1-3). Doubts on the reliability of the previously measured values have emerged in recent heat transfer calculations by Bohn, and quite independently and almost concurrently, from viscosity data by Ejima and Sato for molten Na₂CO₃. In the former it was found necessary to assume viscosities approx. 3.5 times larger in order to bring the modelling calculations into agreement with the observed thicknesses of the flowing salt films. The present work was undertaken to try to resolve this dilemma. The investigation was extended to include some work with eutectics from commercial grade quality carbonates, and these results are also reported.
EXPERIMENTAL

All measurements were made with the high temperature facility at Tohoku University in which the damped oscillational technique and working equations for calculating the viscosities on an absolute basis are used. The viscometer, as seen from Figs. 1 and 2, is computer-coupled for data acquisition and data reduction to final values. For the torsion wire, the Kestin alloy (8% W - 92% Pt) was used. This alloy has a stable constant of elasticity, a low internal friction, and is easily annealed stress free (4,5).

Samples of the eutectic (mol %: Li₂CO₃, 43.5; Na₂CO₃, 31.5; K₂CO₃, 25.0; m.pt. 397°C) were prepared in kg. amounts from Reagent Grade salts, and melted to gain sample homogeneity. To repress decomposition, all transfers were under CO₂ atmospheres. For further pretreatment of samples in the viscometer, see later.

In Fig. 3 measurements for molten NaCl are shown. The performance of the viscometer is thus confirmed to be within 2.5% of the recommended values from the Molten Salts Standard Program (6,8). However when measurements were started with the eutectic, a series of performance problems were encountered. As these appeared unique to work with molten carbonates, the resolution of these were important steps to meaningful results.

Log(visc) vs. $T^{-1}$ Correlation: The temperature - viscosity data for "well behaved" ionic salt systems generally may be expressed by an exponential function of the form:

\[ \text{viscosity} = A \exp \left( \frac{E}{RT} \right) \]

and from this, the correlation:

\[ \log(\text{visc}) = \text{constant} + \left( \frac{E}{R} \right)T^{-1} \]

provides a ready graphical check on the progress of the measurements, i.e., a straight line having a slope of $(E/R)$. In the early stages of the present measurements with the molten eutectic, an apparent failure of this criterion was observed. As seen in Fig. 4, the correlation held well for measurements above 700°C, but failed quite abruptly and dramatically at approx. 700°C. When measurements were extended to lower temperatures, the slope changed as shown from positive to negative values. When the cause for this "failure" was resolved, it was found to be due not to anomalous melt properties, but rather to the limitations of the viscometer. The dimensions of the crucible in this series of measurements were [20mm i.d. x 88mm], and this size is suitable for fluids with viscosities up to $\approx 10$ mPa*s. Apparently in the work with the molten eutectic, this limit was being reached at 700°C, and being exceeded below this temperature. With larger cru-
cibles meaningful measurements could be extended down to 600°C as the lower limit. The physical limitations imposed by the hot zone dimensions precluded further increases in crucible size; the temperature range for the measurements in the present study was limited accordingly.

**Melt Creep:** In the damped oscillational technique, as in this work, the molten salt is virtually hermetically sealed in the (cylindrical) crucible via a tightly fitting cap. The viscosities are derived from measurements of the damping effects of the fluid thus confined on the oscillations of the crucible. With the molten carbonate, it was found that the measured viscosity at each temperature did not remain constant, but continued to vary. Inspection of the crucible "post measurements" showed that the outer surfaces had been wetted by the melt, and, indeed, a small pendant drop of the carbonate was hanging externally on the crucible bottom. This melt creep complication was resolved through a series of steps as follows. **Melt treatment:** The eutectics were rigorously pretreated, as already noted, by heating under vacuum up to the melting point (397°C), and then CO₂ equilibrated by bubbling the gas through the melt for ~12 hr at 700°C. An atmosphere of [helium with 50 Torr CO₂] was used in the viscometer during the measurements. This CO₂ partial pressure is larger than the equilibrium dissociation pressures of molten carbonates at these temperatures and yet less than the pressures that introduce instability to the oscillations of the crucible. In this way the melt compositions were effectively held invariant. **Gold plating:** To minimize wetting by the molten carbonate, the nickel crucible surfaces were gold plated. **Venting:** Through a series of test measurements, it was observed that the melt creep occurred principally in the initial stages of a measurement series, i.e., as if melt degassing was occurring, and this apparently led to a forced "gushing" of the melt through the (machine threaded) seal. Accordingly, two small holes as vents were drilled in the crucible cap. The "vented cap" modification proved very effective in minimizing this "gushing" and was used throughout the measurements reported herewith.

The overall weight loss from the crucible was thus minimized to 0.3% or less. Corrections for this were made in the iterative calculations of viscosities.

A further correction, namely the "meniscus effect correction", has been quantitatively examined by Brockner, Törklep, and Øye (10). Under the conditions used in the present study (refer: above), the uncertainties due to this possible error source appear to be less than 2%, i.e., well within the overall accuracy limits of ±3% for the present measurements.

**RESULTS AND DISCUSSION**

Table 1 lists the measured viscosities for Reagent Grade ter-
nary carbonate eutectic. Each value is the average of 4 - 6 determinations. Measurements were limited to $= 650^\circ C$ as the lower limit so as to stay well above the cut-off of $600^\circ C$ (see, earlier). The correlation from this data set, is:

$$\text{visc(mPa.s)} = 0.10120 \exp(33400/RT)$$

where $R = 8.3143 \text{ J K}^{-1}\text{mol}^{-1}$. Use of this for extrapolations down to $500^\circ C$, and lower receives firm support from the linearity of the $[\log(\text{visc}) - T^{-1}]$ criterion.

In Fig.5, these results are compared with the measurements reported earlier by Janz and Saegusa(11). The confidence level in the present work is high. The problem, thus, is to understand the factors in the earlier work that led to such markedly lower values.

In the earlier work, melt densities (in the calculations) were estimated from single salts data and theoretical principles. In the present work, measured values(12) were used. The estimated densities would lead to viscosities $\approx 10\%$ lower than the correct values.

A "voids effect" as a possible error source suggests itself directly from a result found in the present study, namely the need for the "vented cap" for measurements with the carbonate eutectic. The adherence of the gases on the interior crucible walls (as a firmly adsorbed gaseous film) would lead to a "voids effect". Since a radius larger than the actual radius of the melt is now being "input" into the working equations, the calculated viscosities would be smaller than the true viscosities. Modelling calculations (based on the parameters of the viscometer in the present work) show that for voids equivalent melt radius decrease of $\approx 20\%$, the calculated viscosities would be $\approx 65\%$ lower than the true (correct) values.

Additional factors as possible error sources could be listed, but the magnitudes cannot be estimated quantitatively and further discussion is deferred accordingly. From the preceding considerations, it appears that the disagreement can be resolved in large part through the possible presence of a firmly adsorbed gaseous film on the inner crucible surface, and that this "voids effect" undoubtedly escaped detection in the earlier study.

As stated earlier in the communication, measurements were extended to eutectics from commercial grade quality carbonate salts (overall purity: 98.4%, based on carbonate content). Without the CO$_2$ equilibration of these (see: melt treatment), meaningful measurements were not possible. After these were CO$_2$ equilibrated, the viscosities were virtually the same as the values found for the Reagent Grade ternary carbonate eutectic herewith (Table 1).
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REFERENCES

1. R.T. Coyle, R.J. Copeland, R.W. Burrows, and R.M. Gaggin, "High Temperature Molten Salts For Use In Solar Thermal Energy Systems". SERI/TR-255-2001 (1983); Solar Energy Research Institute, Golden, CO 80401.
2. M.S. Bohn, H.J. Green, G. Yeagle, J. Siebarth, O.D. Asbell, and C.T. Brown, "Direct Absorption Receiver Experiments And Concept Feasibility". SERI/TR-252-2884 (Oct. 1986); Solar Energy Research Institute, Golden, CO. 80401.
3. M.S. Bohn, J. Solar Energy Eng. (ASME), 107, 208 (1985).
4. J.R. Kestin and J.M. Mosynski, Brown University Report AF891/11 (July, 1958); AFOSR-7N-752, ASTIA Doc. # 201,576.
5. R.S. Marvin, J. Research Nat. Bur. Std., 75A, 535 (1971).
6. K. Törklep and H.A. Øye, J. Phys. E. Sci. Inst., 12, 875 (1979).
7. T. Ejima, K. Shimakage, Y. Sato, H. Okuda, N. Kamada, and A. Ishigaki, Nippon Kagaku Kaishi, 6, 961 (1982).
8. G.J. Janz, J. Phys. Chem. Ref. Data, 9(4), 791 (1980).
9. G.J. Janz, T. Yamamura, and M. Hansen, MSDC-RP1, pre-publication results (1986).
10. W. Brockner, K. Törklep, and H.A. Øye, Ber. Bunsenges. Phys. Chem. 83, 1 (1979).
11. G.J. Janz and F. Saegusa, J. Electrochem. Soc., 110, 452 (1963).
12. A.T. Ward and G.J. Janz, Electrochimica Acta, 10, 849 (1965).
Fig. 1. High Temperature Viscometer Facility

1: gas purifier
2: resistance furnace
3: guides
4: recording device
5: data processing
   computer
6: Mirror
7: Crucible

Fig. 2. Iterative Calculation Of Viscosity

Start

Define initial value \( \eta_1 \)

Calculate \( P \)

Calculate \( Z \)

Calculate \( \eta_{i+1} \)

Is \( |\eta_{i+1} - \eta_i| < \epsilon \) ?

YES

Stop

NO

Table 1. Eutectic Viscosity: Measured Values.

| \( T \) (K) | Viscosity (mPa*s) |
|------------|------------------|
| 922.6      | 8.058            |
| 972.2      | 6.326            |
| 1021.9     | 5.090            |
| 1071.5     | 4.290            |
| 1122.1     | 3.635            |
| 1172.1     | 3.148            |
| 970.9      | 6.184            |
Fig. 3. Comparisons of NaCl Measurements

Shown: curve 1, (6,8); curve 2, (7); curve 3, this work; curve 4 [inset], predicted (9).

Fig. 4. Eutectic Viscosity.

Fig. 5. Comparisons with Previous Work.