Viscosities of Molten Alkali Carbonates

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Viscosities of Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, Rb$_2$CO$_3$, and Cs$_2$CO$_3$ have been measured by using the oscillating method. Experiments were carried out under He containing 50mPa of CO$_2$ to prevent the decomposition of the carbonates in the temperature range up to 1230K. Isothermal viscosity decreased with increasing cationic radius except the relationship between K$_2$CO$_3$ and Rb$_2$CO$_3$, and the viscosity of Li$_2$CO$_3$ seems lower than that of expected values. Activation energy for viscous flow shows minimum for K$_2$CO$_3$. These phenomena were discussed based on the free space among the constituents and the polarization of anion by small cation. Furthermore, the factors which govern the viscosity of molten salts were discussed by comparing the behavior of other typical molten salts.

[Keywords: viscosity, oscillating method, molten salt, carbonate, activation energy, polarization]

5種類の炭酸塩、Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, Rb$_2$CO$_3$, Cs$_2$CO$_3$について、回転振動法を用いて粘度を測定した。実験は炭酸塩の分解を防ぐために、50mPaのCO$_2$を混合したHe雰囲気を用い約1230Kまでの温度範囲で行った。粘度は全体としてはカチオン半径の増加と共に減少したが、Li$_2$CO$_3$の値はNa$_2$CO$_3$の値に近く、またK$_2$CO$_3$とRb$_2$CO$_3$の間で逆転が認められた。粘性流動の活性化エネルギーはK$_2$CO$_3$において最小となった。このような現象を主として構成粒子間の自由空間の大きさと小さなカチオンによるアニオンの分極効果に関連して考察し、さらに他の典型的な溶融塩との比較を行うことにより、溶融塩における粘性挙動を支配する因子について検討を加えた。

1. INTRODUCTION

Molten carbonates have attracted a great deal of attention because of the application for molten carbonate fuel cell. Therefore, it is important to study the thermophysical properties of molten carbonates. However, big discrepancies are sometimes found in previous works, for example, on the viscosities of molten Li$_2$CO$_3$, Na$_2$CO$_3$, and K$_2$CO$_3$[1,2].

As the viscosity is a fundamental thermophysical property and reflects the microscopic structure of the liquids, it is important to study the viscosity for both the academic interest and the industrial applications. The factors which govern the viscous flow of condensed matter are, for example, bonding force, molar volume and free space among the constituents, and the structural change etc. Therefore the viscosity of molten carbonates is considered to be related to the coulombic force between the cation and anion because most of molten salts including carbonates are basically ionic melts. As the alkali carbonates have large complex anion compared with alkali halides, it is so interesting to study the relationship between the viscosity and the cationic radius.

In this work, it was planned to measure the viscosity of all the molten alkali carbonates including Rb$_2$CO$_3$ and Cs$_2$CO$_3$ precisely because it is important to know their behavior on the viewpoint of the order of atomic number of cation for understanding the viscous flow of the carbonate melts which have divalent and large triangular anion. Furthermore, it is also important to make the above difference between the previous works clear.

2. EXPERIMENTAL

2.1 Crucible for Carbonates

The method used for viscosity measurement in this work was oscillating method using cylindrical crucible. Molten alkali carbonates are very erosive because of its basic and oxidative properties. Then the container material is limited. It is known that gold

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alloy is stable against the molten carbonates. Janz[1]
used the double crucibles system for viscosity mea-
surement in which an inner crucible was made of
Au-Pd alloy with thin wall. However, it is difficult to
make a whole crucible of Au-Pd alloy and to keep
precise dimension because it is expensive and very soft.
Nickel is also known as a relatively resistant material
for oxidation and is used as the electrode material for
molten carbonate fuel cell. Furthermore dimension
stable crucible with thick wall is easily available. How-
ever, nickel is essentially less noble metal. Therefore,
authors tried to plate gold on the nickel. About 50μm
of gold layer was electroplated on the nickel crucible.
The gold plated nickel crucible showed sufficient
resistance against the molten carbonates although the
gold color turned to white by annealing at about
1250K under Ar atmosphere due to the diffusion of
gold into nickel, and turned to somewhat green-black
color by the oxidation after melting the carbonates.
The crucible is cylindrical and has screw outside to
connect with the cap made of nickel which is also
connected with the stainless steel rod. Typical dimen-
sion of the crucible used in this work was about 20mm
in inner diameter and 80mm in depth, respectively.
Inner diameter at high temperature was corrected by
using the equation of expansion coefficient[3].

2.2 Viscometer

Whole apparatus of the oscillating viscometer
used is shown in Fig.1. The crucible is connected to a
stainless steel rod and suspended by a thin Pt alloy wire
through a mirror block and an inertia disk made of
aluminum. The furnace consists of three parts which
were Kanthal wire wound furnaces and controlled
independently to obtain excellent uniformity of the
temperature. The temperature was kept within 0.5K
over the whole length of the crucible. Furthermore, the
furnaces were controlled to obtain the temperature
profile slightly higher at the top of crucible than at the
bottom to prevent the convection flow in the melt. The
atmosphere in the apparatus was dehydrated He con-
taining CO$_2$ up to 5kPa to prevent the decomposition
of the carbonates. The reason for the level of CO$_2$
concentration is as follows; Higher concentration of
CO$_2$ is more effective to prevent the decomposition.
However, the viscosity of CO$_2$ is larger than that of He
and higher concentration of CO$_2$ makes the oscillation
unstable, especially at higher temperatures. Even such
a low concentration of CO$_2$ was considered to be suf-
ficient based on the thermochemical calculation.

2.3 Oscillating system and calculation

The oscillation of the crucible is attenuated by
the viscosity of the melt contained. Oscillating system
in the viscometer is shown in Fig.2.
The inertia disk made of aluminum has most of the moment of inertia in the oscillating system and also acts as the oscillation initiator. Current and voltage coils installed above and under the disk make the rotational force to the disk to twist the Pt alloy wire. After several swing motion, the system starts the oscillation with decay. To detect the oscillation, He-Ne laser and two detectors of phototransistor were used. The light from the laser is reflected by the mirror block connected with the crucible and passes through on the detectors to count the time intervals. In a period of the oscillation, four time intervals were measured in the resolution of 0.1 ms by using 10 kHz pulse generator. 20 sets of time intervals were taken in a measurement, and the period and logarithmic decrement of the oscillation were determined from the data by using the approximation method, in which the error introduced is only $10^{-3}$ to $10^{-5}$% in the range of actual logarithmic decrement for the measurement, developed by authors as described in previous papers[4,5]. The stability of the oscillation was excellent, for example, the standard deviation of the period determined in a measurement was 0.1-0.2 ms, and the reproducibility of the data was also very good. The period and logarithmic decrement obtained were used for the calculation, which was based on Roscoe’s formula[6], of the viscosity. In the calculation, independent physical parameters other than above values measured are required. Those are the mass and density of the melt as a function of the temperature, radius of the crucible corrected by expansion coefficient, moment of inertia of the oscillating system and the logarithmic decrement for empty crucible. The two latter depend on the temperature because of the expansion of the crucible and the increase of viscosity of the atmosphere, then they were determined for individual crucible up to working temperatures to express as a function of the temperature.

To confirm the reliability of present viscometer, measurements were carried out for the distilled water and the mercury as shown in Table 1 with literature values[7]. The satisfactory results were obtained.

2.4 Chemicals

Although alkali carbonates are stable chemically in the atmosphere at room temperature, they may contain the oxide, hydroxide and moisture. Therefore following procedures were used for the purification; The carbonate was fed into 99.5% Al2O3 crucible and melted under vacuum to remove the trace of moisture completely. This procedure may cause some decomposition not only of the hydroxide but also of the carbonate. Then dry CO2 was injected into the melt to convert the resulted oxide to the carbonate. The big crystal solidified was fed into the crucible and was used for the measurement.

3. RESULTS

The viscosities of molten Li2CO3, Na2CO3, K2CO3, Rb2CO3 and Cs2CO3 obtained in this work are shown in Fig.3 with literature values[1, 2].

![Viscosity measured in this work with literature values.](image)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temp./K</th>
<th>obtained /mPa s</th>
<th>Literature[7] /mPa s</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>289.5</td>
<td>1.095</td>
<td>1.101</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>293.6</td>
<td>1.010</td>
<td>0.992</td>
<td>+1.8</td>
</tr>
<tr>
<td></td>
<td>296.6</td>
<td>0.927</td>
<td>0.924</td>
<td>+0.3</td>
</tr>
<tr>
<td>Mercury</td>
<td>288.4</td>
<td>1.578</td>
<td>1.582</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>305.0</td>
<td>1.497</td>
<td>1.489</td>
<td>+0.5</td>
</tr>
</tbody>
</table>
Temperature ranges of the measurements were from their melting points to about 1230K except Li$_2$CO$_3$ which has highest decomposition pressure among them, and the maximum temperature was limited to 1198K for Li$_2$CO$_3$. The results for all the melts show good Arrhenian linear relationship. It was considered that the measurements were carried out under good condition, for example, no decomposition of the carbonates because the negligible loss of sample mass and the stable oscillation were found. Table 2 also shows the equations of the viscosity as a function of the temperature. The densities used for the calculation were taken from Spedding’s work[8] for Li$_2$CO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$, and from authors’ previous work for Rb$_2$CO$_3$ and Cs$_2$CO$_3$[9]. The total error accompanied by the measurements was estimated within 3% by considering the results obtained at room temperature liquids and the uncertainty of all the physical parameters for the measurement.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Equation</th>
<th>Temp. range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$CO$_3$</td>
<td>log $\eta = -0.9691 + 1828/T$</td>
<td>1016−1198</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>log $\eta = -0.6820 + 1459/T$</td>
<td>1141−1234</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>log $\eta = -0.7270 + 1412/T$</td>
<td>1179−1234</td>
</tr>
<tr>
<td>Rb$_2$CO$_3$</td>
<td>log $\eta = -0.7802 + 1491/T$</td>
<td>1153−1233</td>
</tr>
<tr>
<td>Cs$_2$CO$_3$</td>
<td>log $\eta = -0.9875 + 1593/T$</td>
<td>1073−1230</td>
</tr>
</tbody>
</table>

In comparison with literature values, very big difference was found between the data reported by Janz and Vorob’ev[1,2]. They also used the oscillating method, oscillating crucible by Janz and oscillating pendulum by Vorob’ev, and measured for Li$_2$CO$_3$, Na$_2$CO$_3$, and K$_2$CO$_3$ and their binary or ternary mixture melts. The results by Janz show lower viscosities and considerably higher activation energies than present results and Vorob’ev’s results. On the other hand, those by Vorob’ev almost agree with present results although they showed the results as only isothermal lines in their figure. The activation energies obtained in this work are almost similar to that of other typical molten salts as described below. Therefore, the temperature dependence by Janz are considered to be incorrect although the reason why the results by Janz indicated such a large temperature dependence is not yet clear.

4. DISCUSSION

It is interesting to discuss how the viscosity relates to the periodical order of the component ion in similar compounds such as molten salts since the viscosity is a transport quantity and it is difficult to find the general rule for the liquids with simple structure and low viscosity. Therefore, the order of the magnitude of the carbonate viscosity is interesting. Figure 3 showed that the isothermal viscosity decreases with increasing the atomic number of the cation of the carbonate except the relationship between K$_2$CO$_3$ and Rb$_2$CO$_3$. Of course, the atomic number itself is not the direct factor which affects the viscosity. True factor is radius or mass for the case of the cation with same valence. Although it is not necessarily clear in general what is dominant factor, it is widely recognized that the molar volume is considerably effective on the viscosity through the "free space" among the constituents in the liquid. However, it is so difficult to evaluate the free space. It is probably affected by the volume and shape of constituents, bonding force among the constituents, etc.

The combination of divalent carbonate anion and monovalent alkali cation is considered to make moderate coulombic force to form the ionic liquid. If the coulombic force is stronger such as the case of alkaline earth carbonate, the melting point exceeds the decomposition temperature and thus no melt will be obtained under atmospheric pressure. Therefore, it can be said that the molten alkaline carbonate is the system which coheres with coulombic interaction. The cohesive force in the melts should be stronger for the carbonate with smaller cation. Strong cohesive force resists the shear stress by itself, and it probably decreases the free space among the constituents. That is, moderately strong coulombic force is a main factor for increasing viscosity. Present results generally agree well with above consideration in the relationship between the viscosity and the radius of cation. However, it is difficult to explain following two phenomena. First is closed viscosity between Li$_2$CO$_3$ and Na$_2$CO$_3$. Second is a reversal between K$_2$CO$_3$ and Rb$_2$CO$_3$. For the former, the viscosity of Li$_2$CO$_3$ should be much more larger than that of Na$_2$CO$_3$ if above consideration is directly applied. As a reason, the polarization effect by Li$^+$ or similar mechanism may be mentioned. Li$^+$ makes strong electric field due to its smallest radius in the alkali cations. Then it probably polarizes the carbonate anion or takes a stable position near the carbonate anion. Moiseev[10] considered that Li$^+$ preferably coordinated to the center of carbonate anion
although large cation such as K⁺ tends to coordinate to the edge of the anion. These results the reduction of effective electric charge in the melt. Similar phenomena were found in alkali chlorides, bromides and iodides. The surface energy of Li salts showed considerably lower values, and the reason was considered that considerable amount of the coulombic energy was probably lost by the polarization effect. This effect was also found for Na salts but weaker[11]. As the result, it is considered that the viscosity of Li₂CO₃ decreased from hypothetical original viscosity and approached to the viscosity of Na₂CO₃. For the latter, the reversal may be due to the molar volume of K₂CO₃.

Figure 4 shows the density and the molar volume of alkali carbonates at 1200K.

![Graph showing density and molar volume](image)

**Fig.4** Isothermal density and molar volume of molten alkali carbonates at 1200K.

Obviously the density and molar volume of K₂CO₃ are abnormally low and high, respectively. Similar abnormality on the density was also found in other potassium halides[12]. It is not easy to say that the positive deviation of molar volume at the position of K₂CO₃ means abnormally large molar volume because the abscissa of Fig.4 shows simply the cation order and has less physical meaning. However, the density shows distinct abnormality, smallest density, at K₂CO₃. That is, K₂CO₃ has relatively large molar volume. This may be main reason of low viscosity of K₂CO₃ and the reversal in the order with Rb₂CO₃.

Figure 5 shows the viscosities for comparison with other typical molten salts, alkali fluorides[4], alkali chlorides[13], alkaline earth chlorides[14].

![Graph showing viscosity comparison](image)

**Fig.5** Comparison of the viscosities among typical molten salts.

The viscosities of molten carbonates are same order to that of molten alkaline earth chlorides which consist of divalent cation and monovalent anion. In this case, MgCl₂ shows exceptionally lower viscosity. It is well known as a complex formation of MgCl₂⁺ due to very small radius and stronger coulombic force of Mg²⁺, then similar mechanism to Li salts may act in MgCl₂ and the viscosity decreased. Alkali fluorides and chlorides, which consist of monovalent cation and anion, show smaller viscosities although the viscosities of chlorides are smaller than that of fluorides. The common feature of alkali halides is lower viscosity for Li salts although it is so difficult to find the order in magnitude for chlorides in Fig.5. Similar situation is found for the viscosities of alkali bromides and iodides measured by authors[15] although they are not shown in Fig.5 because it makes the figure confused.
due to similar viscosities. Smallest viscosities were found for LiBr, Lil and NaI among all alkali halides. These facts suggest that the strong coulombic cohesive force, in general, makes the viscosity of ionic melt large as mentioned above. However, the cation with further stronger coulombic force such as Li+ makes the viscosity low because of decrease of cohesive force due to, for example, the polarization of anion.

Figure 6 shows the activation energies for viscous flow of the salts mentioned above.

![Activation energies for viscous flow of typical molten salts.](image)

Activation energies shown in Fig.6 almost support a rough general rule that the higher activation energy corresponds to higher viscosity by comparing with Fig.5, for example, K2CO3 shows lowest activation energy in the carbonates. By looking over the results for many molten salts, it seems that the factor which determines the absolute value of the viscosity are considerably complex. And the molar volume and free space among the constituents are probably most important factor in simple molten salts although they are determined by many factors, for example, polarization effect of anion by small cation other than essential coulombic force.

5. CONCLUSION

The viscosities of molten alkali carbonates have been measured precisely by using the oscillating viscometer. The viscosity of each carbonate showed good linear Arrhenian relationship and almost decreased with increasing the cationic radius. However, Li2CO3 showed relatively lower viscosity, and the reversal between K2CO3 and Rb2CO3 was found. The behavior was discussed to understand the viscosity of ionic melts by considering the factors, for example, free space among the constituents in the melts, polarization effects of anion by small cations.

REFERENCES


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