Ultrasonic Velocities of Molten Alkali Silicates

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Temperature and compositional dependencies of ultrasonic velocities on molten alkali silicates have been reviewed. Although compositional correlation equations for the ultrasonic velocities on molten silicates have been previously proposed, the compositional dependency has not been interpreted yet from the viewpoint of the silicate structure. The authors focused on the ultrasonic velocities of molten alkali silicates, closely examined the reported data and have found that there is an identical linear relationship between the adiabatic compressibilities, which are strongly relevant to the ultrasonic velocities, and the molar volumes. This indicates that the molar volume is one of the most significant factors affecting the ultrasonic velocities.

KEY WORDS: ultrasonic velocity; adiabatic compressibility; molten alkali silicate; molar volume; density.

1. Introduction

Ultrasonic velocities of molten alkali silicates have been reviewed. Although compositional correlation equations for the ultrasonic velocities on molten silicates have been previously proposed, the compositional dependency has not been interpreted yet from the viewpoint of the silicate structure. The authors focused on the ultrasonic velocities of molten alkali silicates, closely examined the reported data and have found that there is an identical linear relationship between the adiabatic compressibilities, which are strongly relevant to the ultrasonic velocities, and the molar volumes. This indicates that the molar volume is one of the most significant factors affecting the ultrasonic velocities.

KEY WORDS: ultrasonic velocity; adiabatic compressibility; molten alkali silicate; molar volume; density.
through a buffer rod and are reflected at the interface between the rod and the sample. The reflected pulses come back through the rod to the transducer where acoustic pulses are converted to electrical pulses. A certain transmission of the pulses takes place from the rod to the sample. The pulses transmitted through the interface are reflected back by the reflector, travel through the rod to the transducer and generate delayed electrical pulses in the transducer. These are received, amplified and displayed on the oscilloscope with the first reflected pulses. When the distance between the end of the rod and the reflector is known, the time delay between the pulse reflected at the interface (between the rod and the sample) and the pulse reflected by the reflector gives the desired velocity of ultrasonic waves.

The aforementioned technique is based on a characteristic of ultrasonics that ultrasonic waves reflect at the interface between two different media. When two media 1 and 2 stay in intimate contact at a perfect interface and the normal incident wave comes from medium 1, the reflection coefficient at the interface between two media is given by

$$R = \frac{Z_2 - Z_1}{Z_2 + Z_1}$$  \hspace{1cm} (2)

where $Z_1$ and $Z_2$ are specific acoustic impedance of media 1 and 2. Acoustic impedance is obtained by multiplying density $\rho$ by velocity of ultrasonic waves $v$.

$$Z = \rho v$$ \hspace{1cm} (3)

Of great importance are the acoustic intensity reflection and transmission coefficient, $R_P$ and $T_P$:

$$R_P = |R|^2$$ \hspace{1cm} (4)

$$T_P = 1 - |R|^2$$ \hspace{1cm} (5)

Now, it is assumed that the sample in Fig. 1(i) is molten 50Na$_2$O(mol%)-50SiO$_2$ slag. Let’s consider the optimal materials for the reflector. The values of $\rho$ and $v$ are 2.24×10$^3$ kg·m$^{-3}$ and 2.8 km·s$^{-1}$, respectively, for 50Na$_2$O (mol%)-50SiO$_2$ slag at 1 400 K, giving a longitudinal acoustic impedance of 6.3 MRayls (10$^6$ N·s·m$^{-3}$) where the Rayl (after Lord Rayleigh) is the MKS unit of acoustic impedance. Poor reactive materials for molten silicates may be Al$_2$O$_3$ and platinum, for instance. The values of $\rho$ and $v$ of sintered almina are 3.9×10$^3$ kg·m$^{-3}$ and 10 km·s$^{-1}$ and $\rho$ and $v$ of platinum are 21.62×10$^3$ kg·m$^{-3}$ and 3.26 km·s$^{-1}$, giving a longitudinal acoustic impedance of 40.1 and 70.5 MRayls, respectively. Consequently, when sintered alumina and platinum are used as the reflector materials, the acoustic intensity reflection coefficients $R_P$ can be calculated as 0.73 and 0.84, respectively. This indicates that platinum is somewhat better than sintered alumina as the reflector material for measuring the velocity of ultrasonic waves of molten silicates.

The advantage of pulse echo technique is that the cell design is simpler than that of the pulse transmission technique. However, the technique has a drawback in that the main pulse is more likely to be affected by the trailing pulse generated by incoherent reflections from the surface of the rod.

2.2. Pulse Transmission Technique

This technique is employed for the liquid sample. In this technique, pairs of buffer rods and transducers are used as shown in Fig. 1(ii). Acoustic pulses generated from the upper (or lower) transducer travel through the attached rod, the liquid and the other rod in turn, and are received by the lower (or upper) transducer. The upper rod can be vertically shifted by a distance $\Delta x$, which is measured very accurately by, for instance, a micro screw gauge or a cathetometer. The time required for a pulse to travel from one transducer to another is precisely measured by an oscilloscope. The velocity of ultrasonic waves ($v$) can be calculated by dividing the change in the distance between two ends of the rods ($\Delta x$) by the change in the time of the travel of the ultrasonic pulses ($\Delta t$).

$$v = \frac{\Delta x}{\Delta t}$$ \hspace{1cm} (6)

The velocity of ultrasonic waves can also be determined by measuring the ultrasonic wavelength ($\lambda$) and frequency ($f$), i.e., $v = \lambda / f$.

3. Factors Affecting the Ultrasonic Velocities of Molten Silicates

3.1. Temperature Dependency

Table 1 summarizes the previous studies with respect to the ultrasonic velocities of molten silicates. For all the data except for only one system, velocity decreases with an increase in temperature; for the PbO–SiO$_2$ system, temperature dependencies are negligibly small at least over the measurement temperature range of 200 K. Figures 2–4 show the temperature dependencies of the ultrasonic velocities on 33(mol%)M–67SiO$_2$ and 50(mol%)M–50SiO$_2$ (M = Li, Na and K) in the liquid states. Because of the reasons described in Section 4, the data of Li$_2$O–SiO$_2$ system reported by Bloom and Bockris and the data of Na$_2$O–SiO$_2$ and K$_2$O–SiO$_2$ systems by Shiraiishi et al. were not adopted for Figs. 2–4. It is seen that there are discrepancies among reported data for the K$_2$O–SiO$_2$ system.

3.2. Composition Dependency

Rivers and Carmichael have reported two compositional
correlation equations for the ultrasonic velocities of molten silicates. One of two is the equation proposed by Ernest et al.26) Ernest et al. have made the argument that if a solution mixes without volume change, one can imagine separating the liquid into layers whose thickness is proportional to the volume fraction of each component, \( x_{i,v} \). The total time for an acoustic wave to transverse the system is equal to the sum of the times required to pass through each layer, \( x_{i,v} / v_i \), where \( v_i \) is the sound speed of layer \( i \). Thus

\[
\frac{1}{v} = \sum \frac{x_{i,v}}{v_i} \quad \text{(7)}
\]

Here, \( v_i \) will be referred to as the sound speed coefficient of component \( i \), which is the definition adopted by Ernest et al. for the sound speed in an ideal solution. Rivers and Carmichael8) have derived the values of \( v_i \) for the 13 oxide components from a multiple linear regression fit to Eq. (7) for the 65 liquid compositions at 1 673 K. For instance, the values of \( v_i \) for SiO\(_2\), Li\(_2\)O, Na\(_2\)O and K\(_2\)O are 2 524, 4 265, 2 639 and 1 660 m·s\(^{-1}\), respectively. It may be surprising that the value of \( v_i \) for SiO\(_2\) is relatively small and between the values for Li\(_2\)O and K\(_2\)O. This means that ultrasonic velocity does not seem to be related to the ionicity or covelency of bonding. In fact, this small ultrasonic velocity, i.e., large compressibility for SiO\(_2\) is in accord with the results reported by Laberge et al.27) and Bucaro and Dardy.28) However, the compositional dependency of ultrasonic velocities of molten silicates has not been interpreted yet from the view-

### Table 1. Previous ultrasonic velocity studies on molten silicates.

| Reference number | Authors          | System                      | Number of compositions |
|------------------|------------------|-----------------------------|------------------------|
| 4)               | Nagata et al.    | Na\(_2\)O–SiO\(_2\)         | 3                      |
|                  |                  | K\(_2\)O–SiO\(_2\)         | 2                      |
|                  |                  | PbO–SiO\(_2\)              | 2                      |
| 5)               | Shiraishi et al. | Li\(_2\)O–SiO\(_2\)         | 4                      |
|                  |                  | Na\(_2\)O–SiO\(_2\)         | 3                      |
|                  |                  | K\(_2\)O–SiO\(_2\)         | 4                      |
|                  |                  | Li\(_2\)O–Na\(_2\)O–SiO\(_2\) | 3                      |
| 6)               | Baidov and Kunin| Li\(_2\)O–SiO\(_2\)         | 13                     |
|                  |                  | K\(_2\)O–SiO\(_2\)         | 7                      |
|                  |                  | CaO–SiO\(_2\)              | 11                     |
| 7)               | Bloom and Bockris| Li\(_2\)O–SiO\(_2\)         | 6                      |
| 8)               | Rivers and Carmichael | Li\(_2\)O–SiO\(_2\) | 2                      |
|                  |                  | Na\(_2\)O–SiO\(_2\)         | 2                      |
|                  |                  | K\(_2\)O–SiO\(_2\)         | 2                      |
|                  |                  | Rb\(_2\)O–SiO\(_2\)        | 1                      |
|                  |                  | Cs\(_2\)O–SiO\(_2\)        | 1                      |

Binary and multi component systems

| 9)        | Bockris and Kojonen | Na\(_2\)O–SiO\(_2\)         | 9                      |
|          |                    | K\(_2\)O–SiO\(_2\)         | 6                      |
| 10, 11)  | Matsuzono et al.   | Li\(_2\)O–SiO\(_2\)         | 1                      |
|          |                    | Na\(_2\)O–SiO\(_2\)         | 3                      |

Fig. 2. Temperature dependency of the ultrasonic velocity on 33(mol%)Li\(_2\)O–67SiO\(_2\) and 50(mol%)Li\(_2\)O–50SiO\(_2\) in the liquid states.

Fig. 3. Temperature dependency of the ultrasonic velocity on 33(mol%)Na\(_2\)O–67SiO\(_2\) and 50(mol%)Na\(_2\)O–50SiO\(_2\) in the liquid states.

Fig. 4. Temperature dependency of the ultrasonic velocity on 33(mol%)K\(_2\)O–67SiO\(_2\) and 50(mol%)K\(_2\)O–50SiO\(_2\) in the liquid states.

### Fig. 2.

Temperature dependency of the ultrasonic velocity on 33(mol%)Li\(_2\)O–67SiO\(_2\) and 50(mol%)Li\(_2\)O–50SiO\(_2\) in the liquid states.

### Fig. 3.

Temperature dependency of the ultrasonic velocity on 33(mol%)Na\(_2\)O–67SiO\(_2\) and 50(mol%)Na\(_2\)O–50SiO\(_2\) in the liquid states.

### Fig. 4.

Temperature dependency of the ultrasonic velocity on 33(mol%)K\(_2\)O–67SiO\(_2\) and 50(mol%)K\(_2\)O–50SiO\(_2\) in the liquid states.
point of the structure. One of the reasons why the compositional dependency has not been elucidated yet is that there are large discrepancies among reported ultrasonic velocities of molten silicates.

The authors will focus on the ultrasonic velocities of molten alkali silicates, closely examine the reported data and investigate the relationship between the ultrasonic velocities and the structures.

4. Composition Dependency of Ultrasonic Velocities and Adiabatic Compressibilities on Molten Alkali Silicates

Figures 5–7 show the velocities of the M₂O–SiO₂ systems (M = Li, Na and K) at 1 573 K as a function of the M₂O content. The velocity of the Li₂O–SiO₂ system increases from ca. 2 700 m·s⁻¹ to ca. 3 200 m·s⁻¹ with increasing the Li₂O content from 30 mol% to 60 mol% except for the data reported by Bloom and Bockris.⁷ With respect to the discrepancy between the data by Bloom and Bockris and others, Baidov and Kunin⁶ and Rivers and Carmichael⁸ have pointed out that the alumina buffer rods that Bloom and Bockris used may have been seriously corroded in the melts during the experiment. Corrosion of alumina buffer rods would increase the true wave path length in the melts, leading to an underestimate of the sound speed. The velocity of the Na₂O–SiO₂ system slightly increases from ca. 2 500 m·s⁻¹ to ca. 2 700 m·s⁻¹ with increasing the Na₂O content from 15 mol% to 60 mol% except for the data reported by Shiraishi et al.⁵ The reason for the deviation in the results of Shiraishi et al. is not clear. On the other hand, the velocity of the K₂O–SiO₂ system decreases from ca. 2 400 m·s⁻¹ to ca. 1 800 m·s⁻¹ with an increase in the K₂O content from 20 mol% to 50 mol% except for the value obtained by Shiraishi et al.⁵ which is much higher than other data. They have used an ultrasonic frequency as large as 10 MHz while other researchers have used frequencies less than 4 MHz. As aforementioned, the ultrasonic velocity is generally independent of the frequency of waves, i.e., dispersionless. Dispersion means that the velocity varies with frequency. In fact, dispersion happens at very high frequencies (for example, with thermal phonons near the Brillouin zone boundaries) or for high viscous materials, in which part of the atomic movements cannot follow high frequencies of ultrasounds. In such an unrelaxed region, the velocity increases with an increase in the frequency. In fact, Baidov and Kunin⁶ have measured the velocities at the frequencies of 1 and 4.7 MHz, and have observed the dispersion in the melts of K₂O–SiO₂ having viscosities of the order of magnitude 100 Pa·s. Therefore, it is considered that 10 MHz is the frequency far above the relaxation region of the melt, and Shiraishi et al. have measured an unrelaxed ultrasonic velocity.

In order to discuss the compositional dependency of ultrasonic velocities from the structural viewpoint, adiabatic compressibility obtained by Eq. (1) may have to be considered because compressibility is more directly relevant to the structure rather than velocity. In order to obtain the adiabatic compressibilities, the density values are required. Figure 8 shows the densities of the M₂O–SiO₂ systems (M = Li, Na and K) at 1 573 K as a function of the M₂O content.⁹ Bloom and Bockris,⁷ Shartsis et al.¹⁰ Šašek and Lisý¹¹,¹² Matsuozono et al. and Nagata et al.¹⁲ have used the direct Archimedes method in which

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Fig. 5. Velocities of the Li₂O–SiO₂ systems at 1 573 K as a function of the Li₂O content (mol%).

Fig. 6. Velocities of the Na₂O–SiO₂ systems at 1 573 K as a function of the Na₂O content (mol%).

Fig. 7. Velocities of the K₂O–SiO₂ systems at 1 573 K as a function of the K₂O content (mol%).
platinum or platinum-rhodium bob of known weight is suspended by a wire attached to the arm of a balance, and the bob is immersed in a molten glass specimen in platinum or platinum-rhodium crucible. Heidtkamp and Endell have used the indirect Archimedes method for the Na$_2$O–SiO$_2$ system with lower Na$_2$O content (less than 30 mol% Na$_2$O), in which a molten glass specimen contained in a platinum crucible is weighted while immersed in NaCl melt. They have used the direct Archimedes method for higher Na$_2$O content. Šašek and Kasa have measured the density of 20(mol%)Na$_2$O–SiO$_2$ by two different methods; the direct Archimedes method and the maximum bubble pressure method, to be 2.219 and 2.198, respectively. Inspection of Fig. 8 indicates that the data obtained by Shartsis et al. are lower than the other data for all the three systems. In this study, the compositional dependencies of the densities, $\rho$ (g·cm$^{-3}$), have been derived by the least square fitting of the data obtained by Bloom and Bockris, Šašek and Lisý, Heidtkamp and Endell and Šašek and Kasa using the direct and indirect Archimedes method as follows:

Li$_2$O–SiO$_2$: $\rho$ (g·cm$^{-3}$) = 2.160 + 2.136·10$^{-3}$·x
- 7.798·10$^{-5}$·x$^2$
(20 $\leq$ x $\leq$ 60 mol%Li$_2$O) .......(8)

Na$_2$O–SiO$_2$: $\rho$ (g·cm$^{-3}$) = 2.250 − 2.617·10$^{-3}$·x + 9.345·10$^{-5}$·x$^2$
- 1.180·10$^{-6}$·x$^3$
(20 $\leq$ x $\leq$ 60 mol%Na$_2$O) ...... (9)

K$_2$O–SiO$_2$: $\rho$ (g·cm$^{-3}$) = 2.192 + 3.173·10$^{-3}$·x
- 1.372·10$^{-4}$·x$^2$
(20 $\leq$ x $\leq$ 40 mol%K$_2$O) .... (10)

The above equations are used to estimate the densities so as to calculate the adiabatic compressibilities, as shown in Figs. 9–11.

5. Relation Between Adiabatic Compressibility and Molar Volume

Rivers and Carmichael have discussed the compositional dependence of adiabatic compressibility assuming an ideal solution: Stebbins et al. state that applying a simple ideal mixing model

$$V(T) = \sum \chi_i V_i$$ ..................................(11)

to all existing high-quality volume measurements on silicate melts yields a standard error of the fit of less than 1%. If the volume mixes ideally at pressures other than 1 atm, then
\[ V(P, T) = \sum_i x_i V_i(P, T) \] .......................... (12)

Differentiation with respect to pressure yields
\[ \left( \frac{\partial V}{\partial P} \right)_T = \sum_i x_i \left( \frac{\partial V_i}{\partial P} \right)_T \] .......................... (13)

Prigogine and Defay\(^{35}\) define the compressibility coefficient of an ideal solution as
\[ \beta_i = -\frac{1}{V_i} \left( \frac{\partial V_i}{\partial P} \right)_T \] .......................... (14)

Combining Eqs. (13) and (14) yields
\[ -\frac{\partial V}{\partial P} = V \beta = \sum_i x_i V_i \beta_i \] .......................... (15)

Dividing by \( V \)
\[ \beta = \frac{1}{V} \sum_i x_i V_i \beta_i \] .......................... (16)

\( x_i V_i / V \) is just the volume fraction of component \( i \), \( x_i \). Thus for an ideal solution
\[ \beta = \sum_i x_i \beta_i \] .......................... (17)

and compressibility mixes linearly in volume fraction of the components. Rivers and Carmichael\(^{8}\) have derived \( (\partial V_i / \partial P)_T \) for the 13 oxide components by multiple linear regression of the 65 melt compositions, and have plotted the \( -(\partial V_i / \partial P)_T \) values as a function of the molar volume of each oxide component, \( V_i \). Rivers and Carmichael\(^{8}\) have reported that the \( -(\partial V_i / \partial P)_T \) values monotonically increase with an increase in the \( V_i \) values, and that the data are on an identical curve of \( -(\partial V_i / \partial P)_T \) vs. molar volume irrespective of any oxide component.

However, the inspection of \( -(\partial V_i / \partial P)_T \) vs. \( V_i \) curve reported by Rivers and Carmichael\(^{8}\) presents that the curve is not linear but convex downward. Combination of this fact with Eq. (14) indicates that \( \beta \) may become larger as the molar volume is larger. This prediction is quite reasonable as the component with larger molar volume may have more free space between ions for compression. Therefore, the adiabatic compressibilities of the \( M_2O-SiO_2 \) systems (\( M = Li, Na \) and \( K \)) at 1 573 K are plotted against the molar volumes as shown in Fig. 12. It can be found that there is an identical linear relation between the adiabatic compressibilities and the molar volumes. This indicates that the molar volume is one of the most significant factors affecting the ultrasonic velocity value. The same systems at other temperatures as well as other systems including molten salts will be carefully considered in the future.

6. Conclusions

After the measurement methods of ultrasonic velocities were briefly outlined, previous data of ultrasonic velocities on molten silicates have been reviewed. It has been reported that ultrasonic velocity decreases with temperature for all the molten silicates except for the PbO–SiO2 system. With respect to the compositional dependency, two compositional correlation equations for the ultrasonic velocities of molten silicates have been proposed. However, the compositional dependency of ultrasonic velocities of molten silicates has not been interpreted yet from the viewpoint of the structure.

The authors focused on the ultrasonic velocities of molten alkali silicates, closely examined the reported data and investigated the relationship between the ultrasonic velocities and the structures. The following results have been obtained.

(1) The velocities of the \( Li_2O-SiO_2 \), \( Na_2O-SiO_2 \) and \( K_2O-SiO_2 \) systems increase from ca. 2 700 m·s\(^{-1}\) to ca. 3 200 m·s\(^{-1}\) with increasing the \( Li_2O \) content from 30 mol% to 60 mol%, slightly increase from ca. 2 500 m·s\(^{-1}\) to ca. 2 700 m·s\(^{-1}\) with increasing the \( Na_2O \) content from 15 mol% to 60 mol% and decrease from ca. 2 400 m·s\(^{-1}\) to ca. 1 800 m·s\(^{-1}\) with an increase in the \( K_2O \) content from 20 mol% to 50 mol%, respectively. This means that ultrasonic velocity does not seem to be related to the ionicity or covalency of bonding.

(2) It has been found that there is an identical linear relation between the adiabatic compressibilities and the molar volumes. This indicates that the molar volume is one of the most significant factors affecting the ultrasonic velocity values.

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