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

Ultrasonics are defined as acoustic waves with frequencies above 20 kHz up to around 1 GHz, while audio frequency is from 20 Hz to 20 kHz although, with time, the upper limit has been reduced significantly. Ultrasonic waves have potential application in refining processes. For example, the size and distribution of nonmetallic inclusions in molten steel and the thickness of refractory walls of blast furnace can be estimated by using an ultrasonic inspection meter. Velocity and absorption coefficient of ultrasonic waves have also scientific interest because they are relevant to the thermodynamic and thermophysical properties such as adiabatic compressibility and volume viscosity. Since ultrasonic waves propagate in materials via phonons, the ultrasonic velocity is regarded as the velocity of phonons. According to Debye's equation,¹⁾ the thermal conductivity of insulators is expressed by $\lambda = Cv/3$ where C is the heat capacity per unit volume, v is the phonon velocity, i.e., the ultrasonic velocity, and l is the phonon mean free path. As a result, the ultrasonic velocity allows the phonon mean free path to be evaluated.²⁾

The ultrasonic velocity is generally independent of the frequency of waves used for the measurement. If it is assumed that the propagation of ultrasonic waves proceeds adiabatically and that local fluctuation of liquid density due to the propagation of ultrasonic waves is negligibly small, adiabatic compressibility β_s can be calculated from the determined velocity of ultrasonic waves v with the equation,

$$\beta_s = \frac{1}{\rho v^2} \quad \dots\dots\dots (1)$$

where ρ is the density of the sample. The ultrasonic velocity generally decreases with increasing temperature as long as the coordination structure does not change. This is because thermal motion of the ions leads to an increase in the nearest-

neighbor separation, resulting in an increase in compressibility.³⁾ It has been reported that ultrasonic velocity decreases with temperature for molten slags^{4–11)} and salts,^{12–15)} and many liquid metals.^{3,16,17)} Ultrasonic velocities of liquid metals have been reviewed by Iida and Guthrie.¹⁷⁾ In this paper, previous data of ultrasonic velocities on molten silicates will be reviewed at first. Then, the compositional dependency of ultrasonic velocities of molten alkali silicates will be discussed from the structural viewpoint.

2. Experimental Methods

Prior to introducing the previous data of ultrasonic velocities on molten silicates, the measurement methods of ultrasonic velocities will be briefly outlined. In most cases, high temperature ultrasonic measurements are carried out using a pulse technique. Ultrasonic pulse is generated and detected by a piezo-electric transducer of quartz or BaTiO₃ crystals at room temperature and transmitted to the high temperature section of the furnace through a buffer rod made of fused silica or polycrystalline or single crystalline alumina. The ultrasonic pulse techniques can be divided into four classes (i) pulse echo technique,^{4,10)} (ii) pulse transmission technique,^{5,13,14,18)} (iii) pulse transmission/echo technique,¹⁹⁾ and (iv) interferometric method.^{6–9)} Pulse transmission/echo technique is suited to ultrasonic measurements at high pressure. Interferometric method is a derived form of the pulse echo or transmission technique. Some examples of this method have been explained elsewhere.^{8,18,20)} The principles of pulse echo and transmission techniques are presented together with some basic theories in the following subsections.

2.1. Pulse Echo Technique

A schematic diagram of the apparatus is shown in Fig. 1(i). Acoustic pulses generated by the transducer transmit

Fig. 1. Cell assemblies of (i) pulse echo technique and (ii) pulse transmission technique.

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 by²¹⁾

$$R = \frac{Z_2 - Z_1}{Z_2 + Z_1} \quad \text{..... (2)}$$

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

$$Z = \rho v \quad \text{..... (3)}$$

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

$$R_P = |R|^2 \quad \text{..... (4)}$$

$$T_P = 1 - |R|^2 \quad \text{..... (5)}$$

Now, it is assumed that the sample in Fig. 1(i) is molten 50Na₂O(mol%)-50SiO₂ slag. Let's consider the optimal materials for the reflector. The values of ρ and v are $2.24 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ ²²⁾ and $2.8 \text{ km}\cdot\text{s}^{-1}$ ⁴⁾, respectively, for 50Na₂O (mol%)-50SiO₂ slag at 1400 K, giving a longitudinal acoustic impedance of 6.3 MRayls ($10^6 \text{ N}\cdot\text{s}\cdot\text{m}^{-3}$) where the Rayl (after Lord Rayleigh) is the MKS unit of acoustic impedance. Poor reactive materials for molten silicates may be

Al₂O₃ and platinum, for instance. The values of ρ and v of sintered alumina are $3.9 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ and $10 \text{ km}\cdot\text{s}^{-1}$ ²³⁾ and ρ and v of platinum are $21.62 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ and $3.26 \text{ km}\cdot\text{s}^{-1}$ ²⁴⁾ 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 Δx , 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 (Δx) by the change in the time of the travel of the ultrasonic pulses (Δt).

$$v = \frac{\Delta x}{\Delta t} \quad \text{..... (6)}$$

The velocity of ultrasonic waves can also be determined by measuring the ultrasonic wavelength (λ) and frequency (f), i.e., $v = \lambda / f$.^{18,25)}

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-SiO₂ system, temperature dependencies are negligibly small at least over the measurement temperature range of 200 K.⁴⁾ Figures 2–4 show the temperature dependencies of the ultrasonic velocities on 33(mol%)M₂O–67SiO₂ and 50(mol%)M₂O–50SiO₂ (M = Li, Na and K) in the liquid states. Because of the reasons described in Section 4, the data of Li₂O–SiO₂ system reported by Bloom and Bockris⁷⁾ and the data of Na₂O–SiO₂ and K₂O–SiO₂ systems by Shiraishi *et al.*⁵⁾ were not adopted for Figs. 2–4. It is seen that there are discrepancies among reported data for the K₂O–SiO₂ system.

3.2. Composition Dependency

Rivers and Carmichael⁸⁾ have reported two compositional

Table 1. Previous ultrasonic velocity studies on molten silicates.

Reference number	Authors	System	Number of compositions
4)	Nagata <i>et al.</i>	Na ₂ O–SiO ₂	3
		K ₂ O–SiO ₂	2
		PbO–SiO ₂	2
5)	Shiraishi <i>et al.</i>	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 <i>et al.</i>	Li ₂ O–SiO ₂	1
		Na ₂ O–SiO ₂	3

Fig. 2. Temperature dependency of the ultrasonic velocity on 33(mol%)Li₂O–67SiO₂ and 50(mol%)Li₂O–50SiO₂ in the liquid states.

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

Fig. 3. Temperature dependency of the ultrasonic velocity on 33(mol%)Na₂O–67SiO₂ and 50(mol%)Na₂O–50SiO₂ in the liquid states.

Fig. 4. Temperature dependency of the ultrasonic velocity on 33(mol%)K₂O–67SiO₂ and 50(mol%)K₂O–50SiO₂ in the liquid states.

$$\frac{1}{v} = \sum \frac{x_{i,v}}{v_i} \quad \dots \dots \dots (7)$$

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 SiO₂, Li₂O, Na₂O and K₂O 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 SiO₂ is relatively small and between the values for Li₂O and K₂O. This means that ultrasonic velocity does not seem to be related to the ionicity or covalency of bonding. In fact, this small ultrasonic velocity, i.e., large compressibility for SiO₂ 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-

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 M_2O – SiO_2 systems ($M = Li, Na$ and K) at 1 573 K as a function of the M_2O content. The velocity of the Li_2O – SiO_2 system increases from ca. 2 700 $m \cdot s^{-1}$ to ca. 3 200 $m \cdot s^{-1}$ with increasing the Li_2O 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 Na_2O – SiO_2 system slightly increases from ca. 2 500 $m \cdot s^{-1}$ to ca. 2 700 $m \cdot s^{-1}$ with increasing the Na_2O 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 K_2O – SiO_2 system decreases from ca. 2 400 $m \cdot s^{-1}$ to ca. 1 800 $m \cdot s^{-1}$ with an increase in the K_2O 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 exam-

ple, 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 ultrasonics. In such an unrelaxed region, the velocity increases with an increase in the frequency. In fact, Bidov and Kunin⁶⁾ have measured the velocities at the frequencies of 1 and 4.7 MHz, and have observed the dispersion in the melts of K_2O – SiO_2 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 M_2O – SiO_2 systems ($M = Li, Na$ and K) at 1 573 K as a function of the M_2O content.^{7,22,29–33)} Bloom and Bockris,⁷⁾ Shartsis *et al.*²⁹⁾ and Šašek and Lisý^{30,31)} have used the direct Archimedes method in which

Fig. 5. Velocities of the Li_2O – SiO_2 systems at 1 573 K as a function of the Li_2O content (mol%).

Fig. 6. Velocities of the Na_2O – SiO_2 systems at 1 573 K as a function of the Na_2O content (mol%).

Fig. 7. Velocities of the K_2O – SiO_2 systems at 1 573 K as a function of the K_2O content (mol%).

Fig. 8. Densities of the M₂O-SiO₂ systems (M = Li, Na and K) at 1573 K as a function of the M₂O 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 Endell³²⁾ have used the indirect Archimedes method for the Na₂O-SiO₂ system with lower Na₂O content (less than 30 mol% Na₂O), 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 Na₂O content. Šasek and Kasa³³⁾ have measured the density of 20(mol%)Na₂O-SiO₂ 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.*²⁹⁾ are lower than the other data for all the three systems. In this study, the compositional dependencies of the densities, ρ (g·cm⁻³) have been derived by the least square fitting of the data obtained by Bloom and Bockris,⁷⁾ Šasek and Lisý,^{30,31)} Heidtkamp and Endell³²⁾ and Šasek and Kasa³³⁾ using the direct and indirect Archimedes methods as follows:

$$\text{Li}_2\text{O-SiO}_2: \rho \text{ (g·cm}^{-3}\text{)} = 2.160 + 2.136 \cdot 10^{-3} \cdot x - 7.789 \cdot 10^{-5} \cdot x^2 \quad (20 \leq x \leq 60 \text{ mol\%Li}_2\text{O}) \dots\dots(8)$$

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

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

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

Fig. 9. Adiabatic compressibilities of the Li₂O-SiO₂ systems at 1573 K as a function of the Li₂O content (mol%).

Fig. 10. Adiabatic compressibilities of the Na₂O-SiO₂ systems at 1573 K as a function of the Na₂O content (mol%).

Fig. 11. Adiabatic compressibilities of the K₂O-SiO₂ systems at 1573 K as a function of the K₂O content (mol%).

5. Relation Between Adiabatic Compressibility and Molar Volume

Rivers and Carmichael⁸⁾ have discussed the compositional dependence of adiabatic compressibility assuming an ideal solution: Stebbins *et al.*³⁴⁾ state that applying a simple ideal mixing model

$$V(T) = \sum_i x_i V_i \dots\dots\dots(11)$$

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

$$V(P, T) = \sum_i x_i V_i(P, T) \quad (12)$$

Differentiation with respect to pressure yields

$$\left(\frac{\partial V}{\partial P} \right)_T = \sum_i x_i \left(\frac{\partial V_i}{\partial P} \right)_T \quad (13)$$

Prigogine and Defay³⁵⁾ define the compressibility coefficient of an ideal solution as

$$\beta_i = -\frac{1}{V_i} \left(\frac{\partial V_i}{\partial P} \right)_T \quad (14)$$

Combining Eqs. (13) and (14) yields

$$-\frac{\partial V}{\partial P} = V\beta = \sum_i x_i V_i \beta_i \quad (15)$$

Dividing by V

$$\beta = \frac{\sum_i x_i V_i}{V} \beta_i \quad (16)$$

$x_i V_i / V$ is just the volume fraction of component i , $x_{i,v}$. Thus for an ideal solution

$$\beta = \sum_i x_{i,v} \beta_i \quad (17)$$

and compressibility mixes linearly in volume fraction of the components. Rivers and Carmichael⁶⁾ 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 Carmichael⁸⁾ 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 Carmichael⁸⁾ presents that the curve is not linear but convex downward. Combination of this fact with Eq. (14) indicates that β_i 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 1573 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

Fig. 12. Adiabatic compressibilities of the M_2O - SiO_2 systems ($M = Li, Na$ and K) at 1573 K as a function of the M_2O content (mol%).

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 - SiO_2 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. 2700 $m \cdot s^{-1}$ to ca. 3200 $m \cdot s^{-1}$ with increasing the Li_2O content from 30 mol% to 60 mol%, slightly increase from ca. 2500 $m \cdot s^{-1}$ to ca. 2700 $m \cdot s^{-1}$ with increasing the Na_2O content from 15 mol% to 60 mol% and decrease from ca. 2400 $m \cdot s^{-1}$ to ca. 1800 $m \cdot s^{-1}$ 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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