\[ \sigma_1 = \frac{v_1v_2}{v_1n_1 + v_2n_2} \left( \frac{h_2 - h_2^{PL}}{v_2} - \frac{h_1 - h_1^{PL}}{v_1} \right) \frac{\partial}{\partial n_1} \frac{\partial (\mu_1 - \mu_1^{PL})}{\partial n_1} \]
Soret effect in binary glass-forming oxide melts: theory and its verification

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Soret effect is temperature-gradient-driven mass diffusion in a multicomponent system. This paper reviews the recent progress of understanding the Soret effect in glass-forming oxide melts. A new model, called adjusted Kempers model, is proposed to quantitatively predict Soret coefficients in binary glass-forming oxide melts. The model is verified by experiment and molecular dynamics simulation. In a 11Na$_2$O–89B$_2$O$_3$ (mol%) melt, the difference of the Soret coefficient of Na$_2$O between experiment and theory is 19%. In the nonequilibrium molecular dynamics simulation of CaO–SiO$_2$ glass melts, the Soret coefficient of SiO$_2$ is decreased with SiO$_2$ content and a sign change is observed, which is consistent with the adjusted Kempers model. These results indicate that the adjusted Kempers model is promising. Additionally, this paper reviews the laser-induced Soret effect in multicomponent glasses.

Key-words : Glass, Glass melt, Temperature gradient, Soret effect, Diffusion

1. Introduction

1.1 Soret effect in binary system

Soret effect, discovered by Ludwig$¹$ and tested by Soret,$²$ is temperature-gradient-driven mass diffusion in a multicomponent system. Conceptual image of the Soret effect in binary system with component 1 and 2 is shown in Fig. 1.

The mass flux of component 1 in a binary nonelectrolyte system under a temperature gradient can be written as$³$

\[ J_1 = -\rho[D_M \nabla n_1 + n_1(1-n_1)D_T \nabla T], \]

where first and second terms are concentration-gradient-driven diffusion and temperature-gradient-driven diffusion, respectively, and, $n_1$ is the mole fraction of species 1, $\rho$ is the mass density, $T$ is the temperature, and $D_M$ and $D_T$ are the mutual and thermal diffusion coefficients, respectively. Here, the convection such as natural convection and Marangoni convection is neglected. Under one-dimensional concentration gradient and temperature gradient system, the equation can be simplified as

\[ J_{1,x} = -\rho \left[ D_M \left( \frac{\partial n_1}{\partial x} \right) + n_1(1-n_1)D_T \left( \frac{\partial T}{\partial x} \right) \right], \]

where $x$ is the coordination. At the steady state, the first and second term should be balanced, that is, the flux $J_{1,x} = 0$. Then, the Soret coefficient can be obtained as

\[ \sigma_{\text{soret,1}} = \frac{D_T}{D_M} = -\frac{1}{n_1(1-n_1)} \frac{\partial n_1}{\partial T}. \]

$\sigma_{\text{soret,1}}$ expresses whether the component 1 diffuses toward the hot or cold region and its mole-fraction difference between the hot and cold regions. A positive value of $\sigma_{\text{soret,1}}$ indicates that the component 1 concentrates in the cold region, whereas a negative value indicates it concentrates in the hot region. $\sigma_{\text{soret,1}} = -\sigma_{\text{soret,2}}$ should be valid in the binary system.

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Fig. 1. Conceptual image of Soret effect in binary system. The image on the left side illustrates binary system which has homogeneous composition before applying temperature gradient, and that on the right side illustrates the composition distribution after waiting until the system reaches steady state under temperature gradient.
1.2 Soret effect in silicate melts

Soret effect of silicate melts has been mainly investigated in the field of Earth science.\(^5\)–\(^8\) In 1981, Walker et al. firstly investigated the Soret effect of silicate melts.\(^4\) There are two experimental clues in multicomponent silicate melts; silica (SiO\(_2\)) component is concentrated in the hot side;\(^5\)\(^6\) lighter isotopes are concentrated in the hot side more easily than heavier isotopes.\(^6\)\(^–\)^\(^8\) In 2010, Huang et al. suggested that the Soret coefficient in silicate melts is expressed by an additive function of the mass- and chemical-effect terms. The mass-effect term is expressed as the function of mass, charge, and radius of ion, while the function for the chemical-effect term is unclear. About the mass effect, in 2012, Lacks et al. suggested that the Soret effect of isotopes, called isotope fractionation, arises from classical mechanical effects and that a scaling relation based on Chapman-Enskog theory quantitatively predicts the behavior.\(^8\) The qualitative explanation of the classical mechanical effect is as follows; heavier isotope has a larger momentum than the lighter isotope at the same temperature; therefore, the heavier isotope has longer penetration length than lighter isotope when the isotopes move in a direction from hot region toward cold region. However, chemical factors affecting the Soret effect in silicate melts have not been clarified.

1.3 Motivation and scope of this work

Temperature gradients in industrial glass-melting tanks\(^9\) and glass-melting crucibles would cause the Soret effect, which may lead to the spatial inhomogeneity of the glass melts. The inhomogeneity may affect not only the crystallization behavior of glass melts but also chemical and physical properties of produced glass. If we obtain the Soret coefficient of each component in a given glass melt, we can predict the time evolution of the composition distribution by using advection-diffusion equation containing the term of the Soret effect\(^1\)(\(^1\))\(^6\), which would leads to better quality management of the glass production. Therefore, the theoretical and experimental framework to predict the Soret coefficient would be important for the glass manufacture.

In this review, a new theoretical model for Soret effect in a binary glass-forming oxide melt is derived. Then, the model is verified by experiment and molecular dynamics simulation (MD). Additionally, Soret effect in glass induced by laser heating is summarized.

2. Theoretical model

Soret effect in gaseous system has been formulated by kinetic theory of gases.\(^1\)\(^1\) However, Soret effect in liquid and solid system has not been clarified because of complicated interaction between the diffusion species.\(^1\)\(^2\)–\(^1\)\(^4\) Altora et al. proposed a theoretical model for binary liquid system such as water-ethanol system, where they focus on the activation energy of diffusion.\(^1\)\(^3\) Eslamian et al. used activation energy of viscous flow to predict the Soret coefficient in binary mixtures containing water and organic molecule.\(^1\)\(^4\) Since glass-forming binary oxide melts such as Na\(_2\)O–SiO\(_2\), CaO–SiO\(_2\), and Na\(_2\)O–B\(_2\)O\(_3\) generally have stronger nonideality\(^1\)\(^5\) than molecular liquid such as water-ethanol system,\(^1\)\(^6\) the author and coauthors assumed that thermodynamic stability will mainly contribute to Soret effect.\(^1\)\(^7\)\(^–\)^\(^1\)\(^8\) Kempers derived a thermodynamic equation for the Soret coefficient based on the idea that the partition function in the system becomes the maximum at steady state under a temperature gradient.\(^1\)\(^9\),\(^2\)\(^0\) In 1989 paper,\(^1\)\(^9\) Kempers assumed the two-bulb apparatus, which have equal and constant volumes, as shown in Fig. 2. The system has two components. The bulb A and bulb B are kept to be \(T_A = T' + \Delta T/2\) and \(T_B = T' - \Delta T/2\), respectively. \(T'\) is the average temperature of the two bulbs. \(\Delta T\) is positive value and indicates the temperature difference between bulb A and bulb B.

Kempers assumed that the canonical partition function of the whole system \((Z_{\text{total}})\) will be maximum at steady state under a temperature gradient:

\[
\text{maximum } \{Z_{\text{total}}\} 
\]

Generally, \(Z_{\text{total}} = z_A \times z_B\), where \(z_A\) and \(z_B\) are the canonical partition functions of bulb A and bulb B, respectively. By using the thermodynamic relationship,

\[
Z = \exp \left( - \frac{F}{RT} \right),
\]

where \(Z\) is canonical partition function, \(F\) is the Helmholtz free energy, \(R\) is gas constant, \(T\) is temperature. Condition (4) can be modified to

\[
\text{minimum } \left\{ \frac{F_A}{T_A} + \frac{F_B}{T_B} \right\} 
\]

Constraint requirements are as follows:

\[
N_i^A v_i^A + N_i^B v_i^B = N_i^{\text{total}} \quad (i = 1, 2)
\]

\[
N_1^A v_1^A + N_2^A v_2^A = N_1^{\text{total}} v_1^A + N_2^{\text{total}} v_2^A,
\]

where \(N\) is number of the component, \(v\) is the partial molar volume, \(i\) is the number of component. The Eqs. (7) and (8) express law of conservation of mass and equal volume of each bulb, respectively. By applying the Lagrange’s undetermined multiplier method to Eq. (6), Kempers obtained the equation of the Soret coefficient:\(^1\)\(^9\)

\[
\sigma_{\text{Soret,1}} = \frac{v_1 v_2}{v_1 n_1 + v_2 n_2} \frac{h_2 - h_1}{T n_1 \frac{\partial \mu_1}{\partial n_1}}.
\]
where \( v, h, \) and \( \mu \) are the partial molar volume, partial molar enthalpy, and chemical potential, respectively.

In 2001 paper,\(^{20}\) Kempers modified Eq. (4) to

\[
\text{maximum } \frac{Z_{\text{total}}}{Z_{\text{total}}} = \frac{h_2 - h_1}{v_2} \frac{\mu_1 \mu_2}{\mu_1 \mu_2} \frac{\partial n_1}{\partial n_1}.
\]

where \( ^o \) indicates the reference state. Under this condition, the thermodynamic part of the Kempers model is expressed as

\[
\sigma_{\text{Kempers}} = \frac{v_1 v_2}{v_1 n_1 + v_2 n_2} \frac{h_2 - h_1}{h_2 - h_1} \frac{\mu_1 - \mu_2}{\mu_1 - \mu_2} \frac{\partial n_1}{\partial n_1}.
\]

Kempers said that the reference state (\( ^o \)) is normally taken as ideal gas state of pure component and \( \mu_1 \) includes the chemical potential \( \mu_1^o \) of the reference state.\(^{20}\) When calculating the Soret coefficient of oxide melts by Eq. (11), there are two problems; the value of \( \sigma_{\text{Kempers}} \) apparently depends on setting of the reference state of \( h_2, h_1 \) and \( \mu_1 \); we cannot obtain the value of \( \mu_1 \) because chemical potential is generally measured as the difference from a reference state. The author and co-authors assumed that mixing thermodynamic parameter of the two oxides of liquid state contributes to the Soret coefficient, therefore, they took pure liquid state as the reference state: \(^{17,18}\)

\[
\sigma_{\text{adjusted Kempers}} = \frac{v_1 v_2}{v_1 n_1 + v_2 n_2} \frac{h_2 - h_1}{h_2 - h_1} \frac{\mu_1 - \mu_2}{\mu_1 - \mu_2} \frac{\partial n_1}{\partial n_1}.
\]

where the superscript, \( \text{PL} \), indicates the state of pure liquid, which is reference state in the adjusted Kempers model. The mixing thermodynamic parameters of \( h_2 - h_1^{\text{PL}}, h_1 - h_1^{\text{PL}}, \) and \( \mu_1 - \mu_1^{\text{PL}} \) can be easily obtained from literatures and thermochemical software.

3. Verification with experiment

10Na$_2$O–90B$_2$O$_3$ (mol %) glass was prepared by conventional melt-quenching method using a platinum crucible.\(^{18}\) The glasses was sealed in platinum capsules because the oxide components are easily volatilized. Figure 3(a) shows the sizes of the platinum capsules and the glasses. Schematic view of the experimental system for annealing the sample under temperature gradient is shown in Fig. 3(b). The glass-containing platinum capsule was set as the upper side was hotter than lower side in order to reduce the effect of natural convection. The temperature gradients were within the range from 3.2 to 5.3 K/mm. It was difficult to obtain the same temperature gradient in every experiment.

After annealing the samples under temperature gradient for 90 or 180 h, the platinum capsule was cut at intervals of several millimeters and polished. The mole fraction of the heat-treated glass of each slice was measured by confocal Raman spectroscopy. To determine the mole-fraction, the author and co-authors used the ratio of area of peaks around 776 and 806 cm$^{-1}$, which was assigned to the symmetric breathing vibration of six-membered rings with one BO$_4$ tetrahedron and the symmetric breathing vibration of boroxol rings, respectively. The average glass composition of all the slices was approximately 11Na$_2$O–89B$_2$O$_3$ (mol %). The deviation of the average mole fraction from 10Na$_2$O–90B$_2$O$_3$ (mol %) may be attributed to the heat treatment in the process of filling the glass into the capsule.

The Soret coefficients calculated by Eq. (3) are plotted in Fig. 4. The time evolution of the Soret coefficient was discussed by de Groot\(^{21}\) and Tyrrel.\(^{22}\) Lesheva\(^3\) used the following equation to discuss the time evolution of the Soret coefficient of SiO$_2$ component in silicate melts:

\[
\sigma_{\text{Soret},1}(t) = \sigma_{\text{Soret},1}^\text{steady state} (1 - e^{-t/t}),
\]

Fig. 3. (a) Schematic cross-section view of a typical platinum capsule. (b) Experimental Setup for heat treatment to obtain the Soret coefficient with a vertical furnace. Reproduced from Ref. 18.

Fig. 4. Comparison of the Soret coefficient between the experiment and the adjusted Kempers model. Reproduced from Ref. 18.
Where \( \theta_{\text{steady state}} \) is the Soret coefficient of component 1 at steady state, \( t \) is the heat treatment time, and \( \theta \) is the characteristic time for the Soret coefficient to be 63% of steady state. Here, component 1 and 2 corresponds to Na2O and B2O3, respectively. By fitting the experimental data of 90 and 180 h with Eq. (13), the author and coauthors determined the \( \theta_{\text{steady state}} \) and \( \theta \) to be 5.12 \( \times 10^{-3} \) K\(^{-1}\) and 272 h, respectively. The Soret coefficient calculated by the adjusted Kempers model and thermodynamic parameters \(^{(3)-(25)}\) is \( 6.09 \times 10^{-3} \) K\(^{-1}\). The difference between experiment and theory is 19%, which may be attributed to the Marangoni convection, kinetic factors such as the classical mechanical effect between ions,\(^ {89}\) or measurement uncertainty.

4. Verification with numerical simulation

The advantage of the MD in the study of the Soret effect is that the effect of the natural convection and Marangoni convection can be neglected since the effect of gravity and no boundary can be excluded.\(^ {26}\) The author and coauthors compared the Soret coefficient calculated by nonequilibrium molecular dynamics (NEMD) with that by adjusted Kempers model [Eq. (12)]\(^ {17}\) in the CaO–SiO2 melts. In the NEMD, the interionic potential proposed by Seo et al.\(^ {27}\) was employed because the potential parameter sets can reproduce structures and thermodynamic parameters well. The potential function is expressed as:

\[
V(r) = \frac{1}{4\pi\varepsilon_0} \frac{z_i^2 e^2}{r} + f(b_i + b_j) \exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) - \frac{C_i C_j}{r^6},
\]

where \( z \) is the effective ionic charge, \( \varepsilon_0 \) is the dielectric constant of a vacuum, \( a, b, \) and \( c \) are the characteristic parameters of each ion, \( f \) is the standard force, and \( r \) is the distance between the ion pair (i and j). The first, second, and third term express the coulomb interaction, short-range repulsion, and dispersion force, respectively.

The Leap-frog Verlet algorithm was used to integrate the equation of motion, Ewald sum was used to treat the Coulomb interaction.\(^ {28}\) As shown in Fig. 5, the cubic-shaped simulation box was separated into eight slices. The periodic boundary condition was employed on all three-coordinate directions. The first slice was a cold slice kept at 1800 K, while the fifth slice was a hot slice kept at 2200 K. An linear temperature gradient was produced. The particle number was approximately 12000. The characteristic time for the system to be the 95% steady state was calculated as follows:\(^ {5}\)

\[
\theta_{\text{steady state}} = \frac{|x_{\text{hot}} - x_{\text{cold}}|^2}{\pi D_{\text{Si}}}
\]

where \( x_{\text{hot}} \) and \( x_{\text{cold}} \) denote the coordinates of the hot and cold slice, respectively, and \( D_{\text{Si}} \) is the self-diffusion coefficient of Si. The system was kept under temperature gradient for \( \theta_{\text{steady state}} \) until the system is closed to the steady state. Then the mole fraction distribution of each atom was sampled from \( \theta_{\text{steady state}} \) and 3\( \theta_{\text{steady state}} \).

As shown in Fig. 6, the difference of the Soret coefficient between the NEMD (red plots) and the adjusted Kempers model (blue plots) is almost not dependent on the composition, that is, the values are changed in parallel. Kempers said that there are two factors contributing to the Soret effect: thermodynamic factor from attraction/repulsion and kinetic factor from collision interaction between components in Soret effect. Based on this idea, since the adjusted Kempers model is the thermodynamic model, the difference between the NEMD simulation and the theoretical model may come from the kinetic factor.

The sign of the Soret coefficient in adjusted Kempers model [Eq. (12)] is determined by the term of \((h_2 - h_2^{\text{PL}})/v_2 - (h_1 - h_1^{\text{PL}})/v_1\). Here, component 1 and 2 corresponds to SiO2 and CaO, respectively. The author and coauthors indicate that the \( h_2 - h_2^{\text{PL}} \) and \( h_1 - h_1^{\text{PL}} \) drastically change with the SiO2 content while the change of \( v_2 \) and \( v_1 \) is almost independent on the SiO2 content. Therefore, the main factors to determine the diffusion direction of SiO2 and CaO components are \( h_2 - h_2^{\text{PL}} \) and \( h_1 - h_1^{\text{PL}} \).

5. Soret effect induced by laser-local heating

Steep temperature gradient (~10\(^7\) K/m) can be obtained inside a transparent glass by high-repetition rate ultrafast laser.
laser irradiation.\textsuperscript{29)--31) Such temperature gradient will cause the Soret effect if the temperature of irradiated area is much higher than glass transition temperature. Figure 7(a) shows the case of 50CaO–50SiO\textsubscript{2} (mol\%) after one-spot irradiation.\textsuperscript{32) The optical microscope (OM) image shows the two concentric boundaries. The temperature at the outer boundary should reach around the glass transition temperature during laser irradiation.\textsuperscript{29)--31) Inside the boundary, viscoelastic deformation should occur.\textsuperscript{29)--31) Inside the inner boundary, the temperature should be high enough to diffuse the ions and the glass composition should be modified by Soret effect.\textsuperscript{29}) In this case the concentration of CaO is higher in the outside, i.e. cold side and that of SiO\textsubscript{2} is higher around the center, i.e. hot side.\textsuperscript{29)--31} This concentration distribution is consistent with the simulation result at 50 mol\% SiO\textsubscript{2} in the Fig. 6.

The concentrated region (cold region or hot region) of oxide components in binary-component glass melts is summarized below. In 30Na\textsubscript{2}O–70SiO\textsubscript{2} (mol\%), the concentration of Na\textsubscript{2}O on the colder side was 12 mol\% higher than that on the hotter side,\textsuperscript{33) in 15Na\textsubscript{2}O–85B\textsubscript{2}O\textsubscript{3} (mol\%), the concentration of Na\textsubscript{2}O was higher on the colder side,\textsuperscript{34) and in 15Na\textsubscript{2}O–85GeO\textsubscript{2} (mol\%), the concentration of Na\textsubscript{2}O was higher on the colder side.\textsuperscript{35) The laser-induced Soret effect can change glass properties such as refractive index,\textsuperscript{36) luminescence intensity,\textsuperscript{37) and phase separation.\textsuperscript{33) Figure 8 shows secondary electron images of the phase separation induced in a 26Na\textsubscript{2}O–74SiO\textsubscript{2} (mol\%) glass by laser irradiation and post annealing.\textsuperscript{33) In this case, the Na\textsubscript{2}O mole fraction decreases by Soret effect and the composition changes from miscible

![Fig. 7. OM images and element distributions after laser irradiation. (a) One-spot irradiation. (b) Two-spot irradiation with a distance of 42.7 $\mu$m between the two focal spots. (c) Two-spot irradiation with a distance of 31.9 $\mu$m between the two focal spots. Reproduced from Ref. 32 with permission from The Optical Society.](image)

![Fig. 8. (a) Scanning electron microscope (SEM) image of the irradiated area of the 26Na\textsubscript{2}O–74SiO\textsubscript{2} (mol\%) glass sample after laser irradiation, heat treatment for 3 h at 575°C, polishing to expose the modified region on the surface, and etching. (b) Magnified image of (a), (c), (d), and (e) Magnified SEM images for heat-treatment times of 3, 12, and 48 h, respectively. The numbers 1 and 2 denote the positions shown in the SEM image in (b). The magnifications of the image shown in (c), (d), and (e) are the same. Reproduced from Ref. 33 with permission from Springer Nature.](image)
region into immiscible one \([xNa_2O-(100-x)SiO_2:x = 1–20.5 \text{ mol} \%]^{39}\).

Sakakura et al. indicated the importance of convection on the Soret effect.\(^{39}\) They succeeded in changing the shape of element distribution by multi spot simultaneous irradiation.\(^{39}\) Kishi et al. reported the Soret effect induced by the continuous-wave-laser irradiation to a steel microsphere inside a 30CaO–10Al_2O_3–60SiO_2 (mol %) glass.\(^{40}\)

6. Conclusion

A new model, called adjusted Kempers model, for the Soret effect in binary glass-forming oxide melts was proposed. Considering the predictive power for the Soret coefficient, the model is promising. It should be future work to verify the model in other glass-forming oxide melts and to predict the composition distribution inside the glass tank and crucible by advection diffusion equation containing term of Soret effect.

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