Redox Equilibria of Tin Ions in Alkali Borate Melts

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アルカリホウ酸塩融体中のスズイオンの酸化還元平衡

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The Sn^{4+} – Sn^{2+} equilibrium in binary sodium borate melts was studied by means of differential pulse voltammetry. The half-wave potentials in the reduction of Sn^{4+} to Sn^{2+} shift to the negative with an increase in Na_2O content and a decrease in temperature. These results indicate that the population of Sn^{4+} increases with an increase in basicity. A linear relation between $\log r$ ($r = [\text{Sn}^{2+}]/[\text{Sn}^{4+}]$) and optical basicities was observed. $\log r$ was also found to depend linearly on thermodynamic basicity, such as $-\log a(\text{Na}_2\text{O})$ where $a(\text{Na}_2\text{O})$ denotes the activity of Na_2O in melts.

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1. Introduction

Oxidation-reduction equilibria of multivalent metal ions in glass melts depend on the temperature and duration of the melting procedure, the melt composition and the ambient oxygen pressure. Recent investigations of refining agents and the redox equilibria of refining ions, especially in relation to the temperature dependence of the concentration ratio of redox pair ions, are issues of great importance for the glass industry. Among them, tin is also used as float bath in the float method. It is important to know the redox equilibria of tin in glass melts. Electrochemical methods have been successfully applied to the redox equilibria in glass melts.^{1)–10)} In particular, Rüssel et al. measured the half-wave potentials of reductions for various ions by square-wave voltammetry.^{7)–9)} We also have examined the half-wave potential of Cr^{4+} , Sb^{5+} and Fe^{6+} ions in borate and silicate melts and explained these redox equilibria in terms of the basicities of the melts. The determination of the redox ratio r ($r = [\text{Sn}^{2+}]/[\text{Sn}^{4+}]$), and examination of the coordination structures around tin ions are also important issues. In this latest study, we have measured the half-wave potentials for the reduction of Sn^{4+} in binary alkali borate melts by differential pulse voltammetry.

2. Electrode reaction

The voltammetry uses three electrodes; i.e., a reference, a working and a counter electrode, in which current (i)–potential (E) curves are recorded during electrolysis.^{2),10)} The reference and working electrode potentials correspond to the following reaction:

Generally, two reduction peaks are observed in i – E curves. Rüssel also observed these two step reactions in an earlier investigation.⁸⁾ These two reductions at the working electrode can be written as:

The present experiment was limited within the first-step reaction, so that the overall reaction is given by:

The voltage, E , the difference between the working and reference electrode potentials is related to the formal potential, E° , under 1.013×10^5 Pa of oxygen as given by:

$$E = E^\circ - (RT/2F) \ln r - (RT/2F) \ln D(\text{Sn}^{2+})/D(\text{Sn}^{4+}) \quad (5)$$

Here, R , F and D are gas constant, Faraday constant and

diffusion coefficient, respectively. When gas–liquid equilibrium was attained and the diffusion coefficient of Sn^{4+} is the same as that of Sn^{2+} , the formal potential in Eq. (5) can be replaced by the half-wave potential, $E_{1/2}$, which can be expressed in terms of the following equation:

$$E_{1/2} \doteq (RT/2F) \ln r \quad (6)$$

3. Experimental

One mol% samples of SnO or SnO_2 were melted in a platinum crucible with desired quantities of boric acid and alkali carbonate at 1273 K in a pretreatment furnace. SnO was used only in the determination of the time required to attain the constant peak potential. After measurements were taken, several melts were quenched to form glasses and offered for chemical analyses. The concentrations of sodium ions were determined by flame spectrophotometry. The tin-ion content was determined by atomic absorption.

The cell assembly was the same as that shown in a previous paper⁵⁾ with the oxygen gas introduced at the bottom of the reaction tube. The potential was scanned at a rate of 10 mV/s. The height and duration of a pulse were set at 10 mV and 50 ms, respectively, and the time between

Fig. 1. Relation between the peak potential and duration of heat treatment in $25\text{Na}_2\text{O} \cdot 75\text{B}_2\text{O}_3$ melt at 1163 K.

(○) from SnO , (●) from SnO_2 .

pulses at 100 ms. In a preliminary experiment, the time required for the determination of the half-wave potential was examined. Figure 1 represents the time lapse to attain the constant potentials in a $25\text{Na}_2\text{O} \cdot 75\text{B}_2\text{O}_3$ melt. After about 24h the two initial values from the reduced (SnO) and oxidized (SnO_2) sides coincided, so that the half-wave potential was only determined after 24h had elapsed from when the cell assembly was inserted into the furnace.

4. Results and discussion

The analytical compositions of two freely selected glasses determined by the three measurement procedures for each sample were $28.9\text{Na}_2\text{O} \cdot 71.1\text{B}_2\text{O}_3$ ($30\text{Na}_2\text{O} \cdot 70\text{B}_2\text{O}_3$) and $19.1\text{Na}_2\text{O} \cdot 80.9\text{B}_2\text{O}_3$ ($20\text{Na}_2\text{O} \cdot 80\text{B}_2\text{O}_3$). The numerical values in parentheses are the batch's composition. The loss of alkali oxide seems to increase with an increase in the initial content. However, it was not that large as to preclude the composition of the melts being represented by batch composition. The total loss of tin-ion content was 2.6% on average among the four glasses. Moreover, the total tin-ion concentration did not change during experiments.

The temperature dependence of the half-wave potential is shown in Fig. 2. The half-wave potentials at 1230 K are also plotted in Fig. 3 as a function of sodium-oxide content. As can be seen from this figure, the half-wave potentials shift toward the negative with an increase in Na_2O content and with a decrease in temperature. Log r derived from Eq. (6) is shown as a function of temperature in Fig. 4. Pyare and Nath, determined r in alkali silicate glasses by the chemical analysis of quenched glasses whose melts equilibrated at 1673 K in air. They showed r decreased with an increase in basicity.¹¹⁾ The r of glasses can be examined in terms of the complex formation of Sn^{4+} and Sn^{2+} ions. Through the application of Mössbauer spectroscopy, Dannheim and Frey, and Paul et al. determined the coordination numbers of Sn^{2+} and Sn^{4+} .^{12),13)} Sn^{4+} ions were found to have a strong tendency to form complex ions by coordinating with free oxide ions (O^{2-}) accompanying alkali ions especially in basic melts. Six-coordinated Sn^{4+} ions were also observed in acidic melts, while four-coordinated Sn^{2+} ions were observed in basic melts. Thus the following two reactions are thought to occur:

Fig. 2. Temperature dependence of the half-wave potential in $X\text{Na}_2\text{O} \cdot (100-X)\text{B}_2\text{O}_3$ melts.

Fig. 3. Relation between the half-wave potential and melt composition in $X\text{Na}_2\text{O} \cdot (100-X)\text{B}_2\text{O}_3$ melts at 1230 K.

Fig. 4. Effect of melt composition and temperature on the $[\text{Sn}^{2+}]/[\text{Sn}^{4+}]$ concentration ratio (r) in $X\text{Na}_2\text{O} \cdot (100-X)\text{B}_2\text{O}_3$ melts.

Thus, r_{theor} is expressed as the following equation:^{10),14)}

$$\begin{aligned} r_{\text{theor}} &= \frac{[\text{Sn}^{2+}]_{\text{total}}}{[\text{Sn}^{4+}]_{\text{total}}} \\ &= \frac{([\text{Sn}^{2+}]_{\text{free}} + [\text{Sn}^{2+}]_{\text{complex}})}{([\text{Sn}^{4+}]_{\text{free}} + [\text{Sn}^{4+}]_{\text{complex}})} \\ &= K_1[\text{O}^{2-}] (1 + K_3[\text{O}^{2-}]^m) / (1 + K_2[\text{O}^{2-}]^n) \end{aligned} \quad (9)$$

K_1 is the equilibrium constant of Eq. (5). K_2 and K_3 are equilibrium constants of Eqs. (7) and (8), respectively.

If K_2 and K_3 are large enough, $\log r_{\text{theor}}$ can be written as:

$$\log r_{\text{theor}} = \text{const.} - (n-m-1)\log[\text{O}^{2-}] \quad (10)$$

When $n-m$ is greater than 1, r_{theor} decreases with an increase in the concentration of $[\text{O}^{2-}]$, i.e., one of the scales of basicity.

Baucke and Duffy derived a linear relation between r and the theoretical optical basicity.¹⁵⁾ Figure 5(a) represents a relation between $\log r$ and optical basicities. The r at 1300 K was derived by the extrapolation of the data presented in this paper. Analogous to silicate glasses, a linear relation was also obtained in borate melts. However, a direct comparison between borate melts and silicate glasses cannot be substantiated at this stage. Tilquin et al. have proposed that chemical changes during the cooling or dissolution of the glass for chemical analysis in aqueous media should also be

Fig. 5. (a) Relation between $\log r$ and optical basicity. (b) Relation between $\log r$ and pO values at 1300 K.

considered.¹⁰⁾ The equilibrium constants, K_1 and K_2 , depend not only on the temperature but also on the difference in the alkali ions as well as the nature of the network of oxides forming. While $n-m$, and therefore r , largely depends on the temperature, Denzumi et al. have proposed a new relation between the half-wave potential and the thermodynamic basicity, i.e., $pO = -\log a(\text{Na}_2\text{O})$, where $a(\text{Na}_2\text{O})$ is the activity of Na_2O in melts.¹⁶⁾ Figure 5(b)

represents the relation between $\log r$ and pO values at 1300 K.²⁾ In this case, a linear relation was also obtained. pO in melts is an acceptable parameter for determining the redox equilibria in melts rather than optical basicity, which is in principle independent of temperature.

5. Conclusion

The half-wave potential in the reduction of Sn^{4+} to Sn^{2+} in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ melts was examined by means of differential pulse voltammetry at various temperatures. The half-wave potential was observed to shift to the negative with an increase in Na_2O content and a decrease in temperature. These results indicate that the population of Sn^{4+} increases with an increase in basicity. A linear relation between $\log r$ ($r = [\text{Sn}^{2+}]/[\text{Sn}^{4+}]$) and optical basicities was observed. Moreover, $\log r$ could be expressed by thermodynamic basicity, such as $pO = -\log a(\text{Na}_2\text{O})$, where $a(\text{Na}_2\text{O})$ represents the activity of Na_2O in the melts.

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