

IRON REDOX EQUILIBRIUM AND DIFFUSIVITY IN MIXED ALKALI-ALKALINE EARTH-SILICA GLASS MELTS

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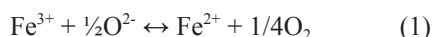
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Dependence of redox behavior and diffusivity of iron on temperature and composition was studied in mixed alkali-alkaline earth-silica glass melts by means of square wave voltammetry (SWV). The voltammograms showed that irrespective of $K_2O/(Na_2O+K_2O)$ the peak potential due to Fe^{3+}/Fe^{2+} moved toward negative direction with temperature decrease and the peak current showed a strong dependence on frequency at constant temperature. Iron diffusion coefficient versus melt viscosity showed a good linearity. The compositional dependence showed that the peak potential shifted to the positive direction with increase of K_2O but a typical mixed alkali effect occurred in iron diffusion either at constant temperature or at constant viscosity.

INTRODUCTION

Iron in technical glasses is inevitable component because it exists as common impurity in natural raw materials as sand, feldspar, dolomite, calcite etc. Iron in glass melts undergoes following redox reaction (1) through which electron transfer between Fe^{3+} and Fe^{2+} occurs and electrons are provided or occupied by oxygen during the reaction. Therefore, Fe^{3+} , Fe^{2+} and physically dissolved oxygen are in equilibrium.



The equilibrium constant $K(T)$ described by the activities or the concentrations of the respective species depends on the temperature, the oxygen pressure and the melt composition. The redox equilibrium state of iron ion is hence very much concerned with some properties of the melt and the final glass, especially heat transfer in infrared region or color of glass products [1].

In the last two decades, voltammetric methods proved to enable the determination of thermodynamic properties and diffusion coefficients of multivalent elements in glass melts. Many studies on the redox behaviors of iron ion in various silicate melts have been performed in situ in the molten state by square-wave voltammetry (SWV) and many thermodynamic [2-7] or diffusion data [8-14] related with the reaction (1) at high temperatures were produced. Among those studies there have been some works in which the compositional dependence of iron redox equilibrium was performed

[5, 8-14]. Especially there was only one study [5] in which the mixed alkali effect in redox behavior of iron ions was approached. However, in that study the iron diffusion, one of the typical kinetic properties in mixed alkali effect was not treated. Alkali-alkaline earth-silica systems are of great importance for the substrate glass of plasma display panel device [15-17]. This paper provides a study on compositional dependence of Fe^{3+}/Fe^{2+} redox equilibrium in alkali-alkaline earth-silica PDP model glass melts doped with 0.1 mol% Fe_2O_3 .

EXPERIMENTAL

The blank melts with the composition in mol.% $69.1SiO_2 \cdot 0.4Al_2O_3 \cdot 9(Na_2O+K_2O) \cdot 6.5MgO \cdot 6.5CaO \cdot 5.3SrO \cdot 1.1BaO \cdot 2.1ZrO_2$ in which $K_2O/(Na_2O+K_2O)$ is varied from 0.25 to 0.75 and the same melts doped with 0.1 mol% Fe_2O_3 were prepared from high purity chemicals. The glass batches of about 300 g were melted at 1550°C in an electric furnace. The bubble free melts homogenized by stirring of Pt/Rh rod was transferred to another electric furnace to perform the measurement of viscosity or SWV.

The melt viscosity was determined by using a vertical precision tube furnace in which a rotating viscometer (RotoVisco "RV30" Hakke Co., Germany) is installed. In the case of SWV measurement, while the prepared melts were maintained at 1400°C in the furnace, the electrodes of electrochemical cell were dipped into the melts. Electrochemical cell for SWV

measurement consists of three electrodes immersed into the melt in Pt/Rh crucible and potentiostat (Model 273A, EG&G, USA) connected with computer. Platinum plate with 10×20 mm and platinum wire with diameter of 1 mm were used as a counter electrode and a working electrode, respectively. The other platinum wire called reference electrode is connected with O²⁻ conducting Y₂O₃-stabilized ZrO₂ (YSZ) material which is contacted with melts and flushed by reference air with known oxygen partial pressure (P_{rO_2} : 0.21 bar) during SWV experiment. Both the experimental equipment and the procedure are in detail described in the reference [7]. During SWV measurement at given temperature the furnace was switched off to avoid disturbance of the measured signal by the current of the heating elements. The measurements took 10-15 seconds depending on the applied frequency. SWV measurements in the present work were performed under following condition: the range of applied potential and frequency, 0 ~ -800 mV and 5~1000Hz. The final voltammogram of each melt at the temperature ranging from 1400°C to 1000°C was obtained by subtracting that of the blank melt from the original recorded voltammogram.

RESULTS AND DISCUSSION

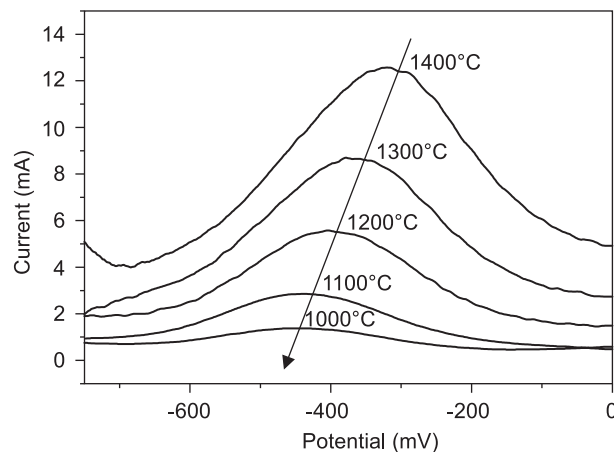
Voltammograms

Figure 1 shows current-potential curves, namely square wave voltammograms at 200Hz in the temperature range of 1000 ~ 1400°C recorded in the melts with $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.25, 0.5$ and 0.75 . In voltammograms one peak due to the reduction of Fe^{3+} to Fe^{2+} (expressed as $\text{Fe}^{3+}/\text{Fe}^{2+}$) is shown clearly at around -400~-300mV irrespective of $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ value. The peak marked by arrow due to $\text{Fe}^{3+}/\text{Fe}^{2+}$ represents a strong dependence on temperature. Based on the E_p -value shown in Figure 1 its temperature dependence is presented in Figure 2. The plot of E_p versus T shows a linear relationship by which the calculation of the standard enthalpy (ΔH^0) and the standard entropy (ΔS^0) for the reaction (1) is possible. The corresponding enthalpy and entropy are contained in Table 1. The movement of E_p to the negative direction with decrease of temperature in Figure 2 means that the equilibrium state of reaction (1) shifts toward the left, namely to the oxidation state. Therefore, Fe^{3+} is preferred at

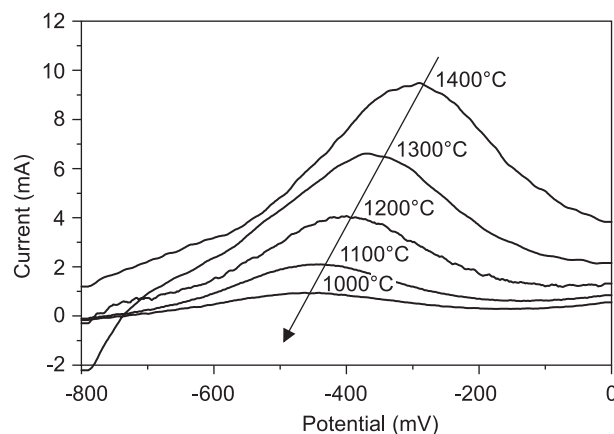
Table 1. Standard enthalpies (ΔH^0) and standard entropies (ΔS^0) for reduction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in melts with $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O}) = 0.25, 0.5$ and 0.75 .

Thermodynamic properties	$\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O})$		
	0.25	0.5	0.75
ΔH^0 (kJ·mol ⁻¹)	96.1	87.9	84.8
ΔS^0 (J·mol ⁻¹ ·K ⁻¹)	38.1	33.9	33.1

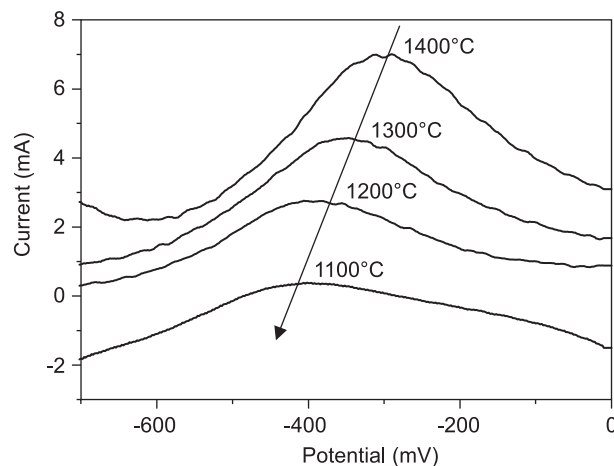
low temperature but with temperature increase it is favorable to exist in the reduced state (Fe^{2+}). In relation to the compositional dependence, with increase of $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ the E_p -value shifts to the positive direction.



a) $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 0.25$



b) $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 0.50$



c) $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 0.75$

Figure 1. Voltammograms of PDP glass melt doped with 0.1mol% Fe_2O_3 in a temperature range of 1400°C to 1000°C at 200 Hz.

Such a tendency is presented in detail in Figure 8 in which E_p -values at different temperature are presented as a function of $K_2O/(Na_2O+K_2O)$.

The voltammograms at 1300°C in the frequency range of 5 ~1000 Hz recorded in the melts with $K_2O/(Na_2O+K_2O)=0.25$ are shown in Figure 3. Although E_p is almost independent of frequency, its corresponding peak current I_p is strongly dependent on the frequency. The other two melts with $K_2O/(Na_2O+K_2O)=0.5$ and 0.75 indicated the same behavior. According to the relationship between I_p and $\tau^{-1/2}$ ($\tau = 1/f$, τ : pulse time, f : frequency), linearity is expected under diffusion controlled reaction and thus the diffusion coefficient (D) can be calculated from the slope. The I_p of the three melts at 1300°C is plotted as a function of $\tau^{-1/2}$ in Figure 4. Table 2 contains diffusion coefficients (D) at different temperature for reduction of Fe^{3+}/Fe^{2+} in melt. D is plotted as a function of temperature in Figure 5. Within the limits of error, the values can be fitted to an Arrhenius type equation, $D = D_0 \exp[-E_D/R_g T]$ where E_D is the activation energy

of the self-diffusion process and D_0 the pre-exponential factor. Comparing the present values of Table 2 with the data of the other silicate melts [8-13], the results belonged to a similar range. The relationship between $\log \eta$ (η : melt viscosity) and $1/T$ in the same temperature range showed also Arrhenius behavior. In Figure 6, it can be observed that an increase of K_2O content leads an increasing viscosity. There have been several studies

Table 2. Diffusion coefficients D (cm^2/s) at different temperature for reduction of Fe^{3+}/Fe^{2+} in melts with $K_2O/(K_2O+Na_2O) = 0.25, 0.5$ and 0.75 .

Temperature (K)	$K_2O/(K_2O+Na_2O)$		
	0.25	0.5	0.75
1673	4.392×10^{-6}	1.369×10^{-6}	1.452×10^{-6}
1573	2.286×10^{-6}	6.849×10^{-7}	7.326×10^{-7}
1473	1.015×10^{-6}	2.743×10^{-7}	2.173×10^{-7}
1373	4.941×10^{-7}	6.033×10^{-8}	5.549×10^{-8}
1273	7.245×10^{-8}	6.795×10^{-9}	1.351×10^{-8}

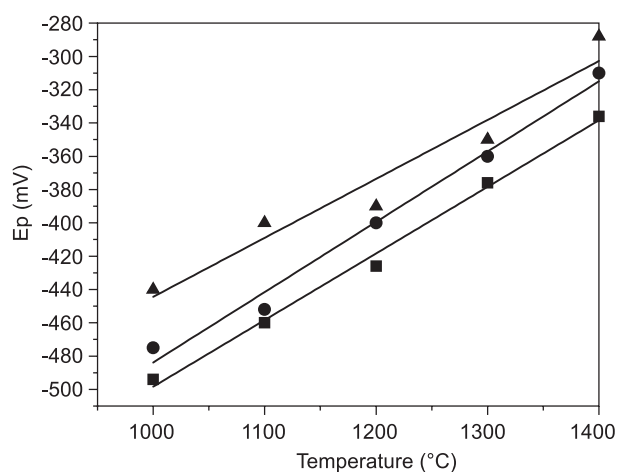


Figure 2. Experimental plot of the peak potential (E_p) at 100 Hz for Fe^{3+}/Fe^{2+} as a function of temperature, $K_2O/(K_2O+Na_2O) = 0.25$ (■), 0.5 (●), 0.75 (▲).

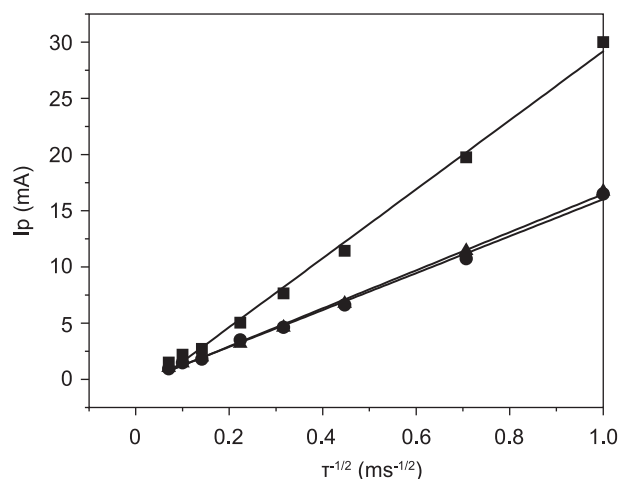


Figure 4. Peak current (I_p) as a function of $\tau^{-1/2}$ at 1300°C for the melts with $K_2O/(K_2O+Na_2O) = 0.25$ (■), 0.5 (●), 0.75 (▲).

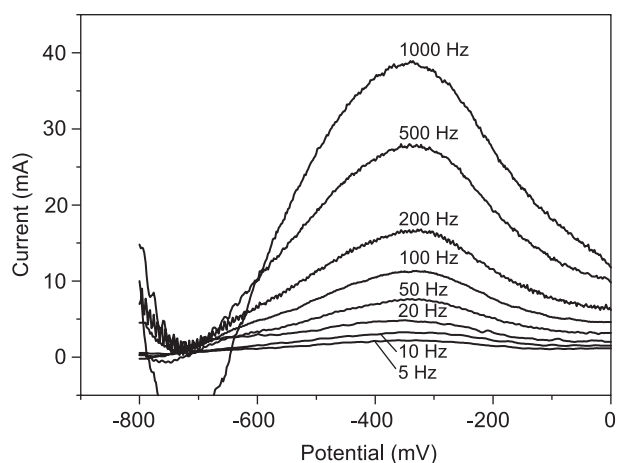


Figure 3. Voltammograms at 1300°C in the frequency range of 5~1000 Hz recorded in melts with $K_2O/(Na_2O+K_2O) = 0.25$.

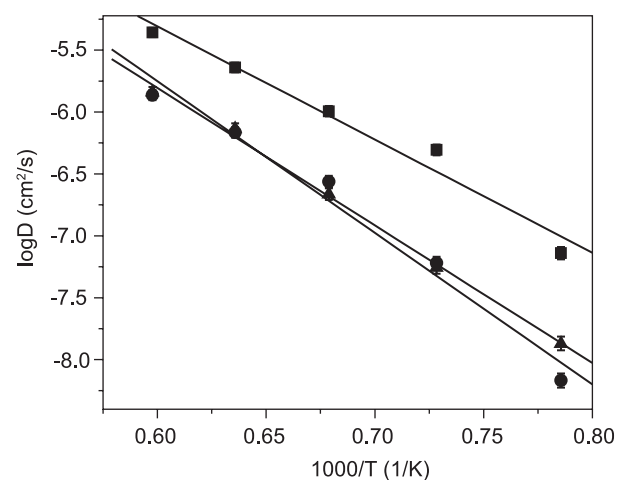


Figure 5. Temperature dependence of the iron diffusion coefficient (D) for the melts with $K_2O/(Na_2O+K_2O) = 0.25$ (■), 0.5 (●) and 0.75 (▲).

[9, 13-14] in which the correlation between iron diffusivity and melt viscosity was treated by the Stokes-Einstein equation:

$$D = kT/6\pi r\eta \quad (2)$$

where k is constant and r is radius of the diffusing species such as iron ion. Figure 7 shows the diffusion coefficient ($\log D$) of iron in the melts as a function of the melt viscosity ($\log \eta$) in the temperature range of 1000~1400°C. For this temperature range $\log D$ depends linearly on $\log \eta$. A proportion between $\log D$ and $\log \eta$ at each temperature for the melts with the same composition is predicted by the Stokes-Einstein equation.

Compositional dependence

Since the present PDP model glasses with 9 mol% total alkali concentration consist of Na_2O and K_2O they belong to typical mixed alkali glasses. The mixed alkali glasses exhibit interesting characteristics, in particular the nonlinear dependence of their properties

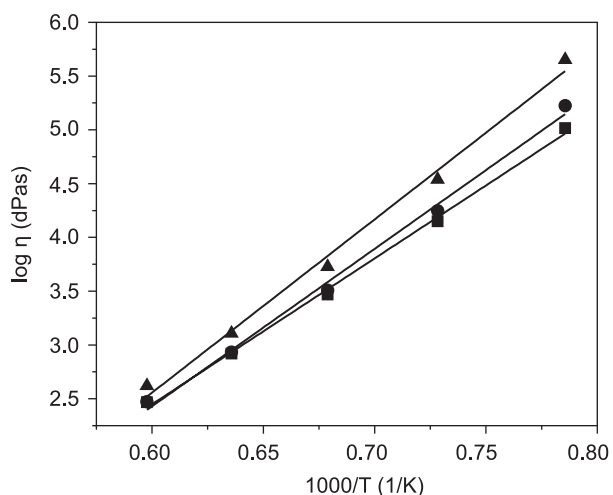


Figure 6. Temperature dependence of the viscosity (η) for the melts with $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.25$ (■), 0.5 (●) and 0.75 (▲).

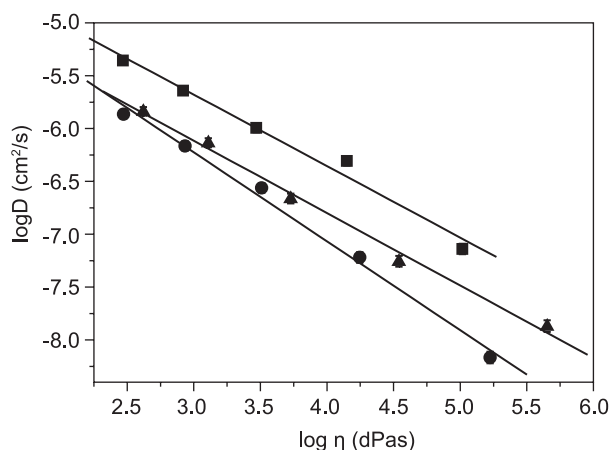


Figure 7. Fe ion diffusion coefficient ($\log D$) as a function of the viscosity ($\log \eta$) for the melts with $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.25$ (■), 0.5 (●) and 0.75 (▲).

on the relative concentration of two network-modifying alkali oxides. The properties of an alkali oxide glass, which depend upon the mobility of the alkali ions such as electrical resistivity, show a strong maximum at an intermediate mixed-alkali composition, when one alkali is replaced by another. This behavior is known as the mixed alkali effect and many relevant experimental data were reviewed in three outstanding papers [18-20]. According to the review papers, the magnitude of the effect increases with increase of radius difference (or difference of field strength) of alkali ion pair and depends on the temperature, and no mixed alkali effect occurs at low alkali concentration less than 10 mol%. Although several theories and models have been developed for the theoretical approach, none of the existing theories has received universal acceptance.

In Figure 8 E_p -values at different temperature are presented as a function of $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$. The compositional dependence of E_p shows no extreme value because the mixed alkali effect is limited in kinetic properties. E_p -values increase simply with increase of K_2O content. The thermodynamic properties, ΔH° and ΔS° of Table 1 show also no extreme value against $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$. As mentioned above, E_p is an indicator of redox reaction: the shift of E_p to the positive value means that the reduction is dominant. In other words, at constant temperature and alkali concentration the equilibrium of redox reaction (1) proceeds to the right hand side with increase of K_2O content. Finally this behavior implies the increase of redox ratio, $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ with increase of K_2O content and thus is opposite to that of Duffy [21] based on basicity which increases with increase of K_2O content in alkali silicate glasses. Therefore such a compositional dependence of E_p in the present study cannot be explained by the glass basicity. Recently two studies on mixed alkali silicate glasses containing antimony ion [22, 23] reported that with increase of K_2O content the oxygen activity decreased in spite of glass basicity increase. The behavior in Figure 8 coincides with that of the above oxygen activity but it

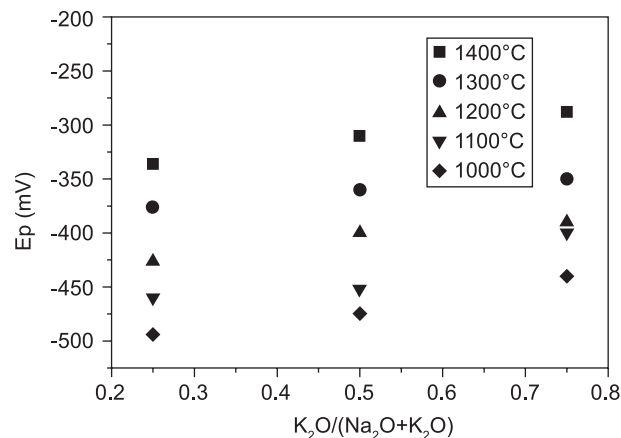


Figure 8. Dependence of peak potential (E_p) at different temperature on $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$.

was not explained why the oxygen activity showed such dependence on $K_2O/(Na_2O+K_2O)$ in mixed alkali melts. According to EPR studies of Rüssel et al. [3, 5], Fe^{3+} existing in the form of $[FeO_4]^-$ tetrahedron prefers small alkali ion, for example Na^+ for electrical neutralization. However, in the case of the mixed alkali melts with high K_2O concentration like $K_2O/(Na_2O+K_2O) > 0.5$, it is a key point to clarify how K ion influences the reduction of Fe^{3+} to Fe^{2+} with the form of $[FeO_6]^{4-}$.

The diffusion coefficient, D is a property depending on ion mobility and, thus the occurrence of the mixed alkali effect is expected in the present melts. Figure 9 exhibits dependence of D at different temperature and E_D on $K_2O/(Na_2O+K_2O)$. There are minima at $K_2O/(Na_2O+K_2O) = 0.5$. Such an effect is also observed in D values at constant viscosity as shown in Figure 10.

CONCLUSION

Redox behavior and diffusivity of iron was studied in mixed alkali-alkaline earth-silicates glass melts with $K_2O/(Na_2O+K_2O) = 0.25, 0.5$ and 0.75 by means of square wave voltammetry (SWV). Correlation between iron diffusion coefficient and melt viscosity was also

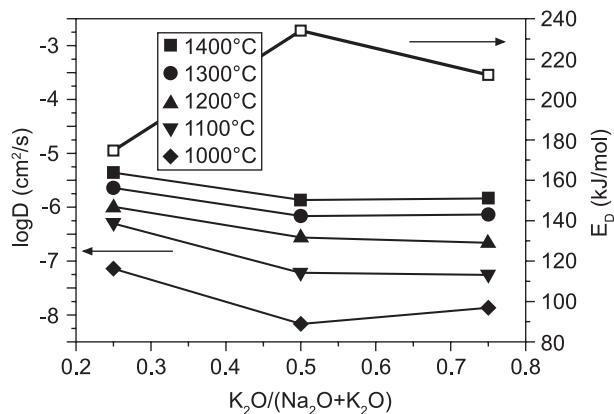


Figure 9. Dependence of diffusion coefficient (D) at different temperature and activation energy (E_D) on $K_2O/(Na_2O+K_2O)$.

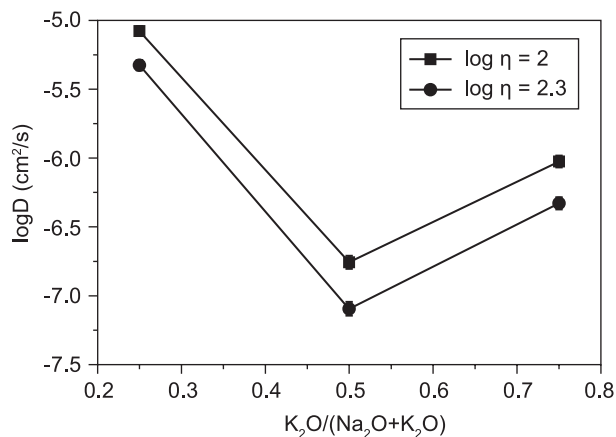


Figure 10. Dependence of diffusion coefficient (D) at constant viscosity on $K_2O/(Na_2O+K_2O)$.

examined. According to voltammograms, in all melts the peak potential due to Fe^{3+}/Fe^{2+} moved toward negative direction with temperature decrease and the peak current showed a strong dependence on frequency at constant temperature. Iron diffusion coefficient versus melt viscosity showed a good linearity based on Stokes-Einstein equation. In relation to the compositional dependence, the peak potential shifted in monotone to the positive direction with increase of $K_2O/(Na_2O+K_2O)$ and its probable cause was regarded as oxygen activity. However, in the case of iron diffusion coefficient there were minima either at constant temperature or at constant viscosity.

Acknowledgements

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