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Effect of alumina on enthalpy of mixing of mixed alkali silicate glasses

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ABSTRACT

The enthalpy of mixing of mixed alkali (Na_2O and K_2O) silicate glasses containing various concentrations of alumina was determined using an ion-exchange equilibrium method. For glasses with a constant alkali concentration, the enthalpy of mixing was found to become less negative with alumina addition. Consistent with our previous results on the enthalpy of mixing of alumina-free mixed alkali silicate glasses, the magnitude of enthalpy of mixing exhibited a good correlation with the molar volume mismatch of the corresponding two single alkali glasses as well as with the extent of conductivity mixed alkali effect, e.g. excess activation energy of conductivity, ΔE. The reduction of the magnitude of the enthalpy of mixing with alumina addition can be attributed to the reduction of non-bridging oxygen and ionic field strength. Combining the present results with results obtained earlier, the magnitude of the enthalpy of mixing for all mixed alkali (Na_2O and K_2O) silicate glasses with and without alumina was expressed by a simple function of a modified Tobolsky parameter, which takes into account the alkali concentration and the difference in cation-to-effective anion distances. The enthalpy of mixing data of the mixed alkali glasses was then compared with reported experimental data on the conductivity of mixed alkali aluminosilicate glasses. What appears to be conflicting experimental data can be understood in terms of the magnitude of the enthalpy of mixing and we can conclude that the mixed alkali effect is closely correlated with the negative enthalpy of mixing.

1. Introduction

Glasses containing two different alkali species exhibit various anomalies in their properties, with the most conspicuous phenomenon being the greatly reduced D.C. electric conductivity of mixed alkali glasses compared with those of the corresponding single alkali glasses. This effect is commonly referred to as the mixed alkali effect and has been observed and evaluated in silicate, borate, germanate, and phosphate glasses [1,2]. While many proposed models can explain parts of the mixed alkali effect reasonably well, none can explain all of the anomalous behaviors. This paper seeks to build upon the previously proposed model invoking the thermodynamics of the mixed alkali glasses [3].

It was previously shown that mixed alkali silicate glasses exhibit a negative enthalpy of mixing by using an ion-exchange method for silicates [3–5] and a calorimetric method for a borate system [6]. This negative enthalpy of mixing was shown to correlate well with the molar volume difference of the corresponding two single alkali glasses with the same total alkali content as well as with the excess activation energy, ΔE, of electric conductivity for a mixed alkali glass system [3]. In the present paper, the effect of alumina addition on the enthalpy of mixing of two alkali silicate glasses was investigated by adding various quantity of Al_2O_3 to alkali-silicate glasses containing Na_2O and K_2O as the alkaline oxide components. Since the addition of alumina to alkali silicate glasses is known to reduce the concentration of non-bridging oxygen, the present study explores the effect of reduction of non-bridging oxygen on the enthalpy of mixing.

Earlier, it was reported by Nariki et al. [7] that the magnitude of the negative enthalpy of mixing of mixed alkali β-ferrites with a β-alumina structure correlates well with the magnitude of the mixed alkali conductivity effect. β-aluminas are known to exhibit a mixed alkali conductivity phenomena similar to glasses [8]. The addition of alumina to alkali silicate glasses reduces the number of non-bridging oxygen and is expected to affect the thermodynamic state of the glass. In fact, it is well known that alumina addition reduces the immiscibility tendencies of alkali silicate glasses greatly [9]. It is also known that the elimination of non-bridging oxygen of sodium silicate glass by the addition of alumina affects the sodium ionic mobility, producing a maximum in D.C. conductivity at the composition corresponding to Na/Al = 1, where no non-bridging oxygen is expected in the glass [10]. The objective of the present paper is to determine the enthalpy of mixing of mixed alkali glasses as a function of alumina addition to alkali silicate glasses and compare the results with previously reported mixed alkali conductivity effects.

The effect of alumina on the mixed alkali conductivity effect of glasses has previously been investigated for some aluminosilicate glass systems. Hayward [11,12] showed a reduction in the mixed alkali conductivity effect in Na_2O–K_2O aluminosilicate glasses with

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increasing Al_2O_3 content. For some glasses without any non-bridging oxygen he observed no mixed alkali effect in D.C. conductivity. On the other hand, Lapp and Shelby [13] showed that Li_2O–Na_2O silicate glasses clearly exhibited a mixed alkali conductivity effect with alumina addition, even when a glass had equal mol% of alkali oxides and alumina, with no non-bridging oxygen expected. A similar trend was shown by Kim [14] for mixed alkali ($Na_2O + K_2O$) silicate glass melts, although the mixed alkali effect of viscosity of alkali silicate glass melts disappeared when SiO_2 is systematically replaced by Al_2O_3 [15]. Additionally, Faivre et al. [16] observed a drastic reduction of the mixed alkali conductivity effect with the addition of Al_2O_3 to mixed alkali ($Li_2O + Na_2O$) phosphate glasses. Thus, at the present time, the effect of Al_2O_3 and non-bridging oxygen on the mixed alkali conductivity effect of glasses and their melts is not perfectly clear. Further investigation of the thermodynamics by an ion-exchange method may resolve this apparent conflict among various data.

Ion-exchange in the aluminosilicate glasses involves the exchanging of one type of alkali ions in the glass structure for another alkali ion using a molten salt, $NaNO_3$ or KNO_3, without altering the glass network. In the present case, four components, Na_2O, K_2O, Al_2O_3, and SiO_2 are contained in a mixed alkali aluminosilicate glass, but the ion-exchange can be considered to take place with no change in the concentration of the non-alkali components. In order to obtain the enthalpy of mixing, ΔH_m, as a thermodynamic quantity, ion-exchange equilibrium will be investigated at a temperature close to T_g for all glasses, where all the glasses can be in meta-stable equilibrium. The obtained enthalpy of mixing then is that of a pseudo-binary system consisting of two single alkali glasses.

2. Experimental procedure

The enthalpy of mixing, ΔH_m, between two alkali-alumino-silicate glasses was determined by establishing ion-exchange equilibria in molten alkali nitrate melts, the same as was done in the previous paper [3] and by Wakabayashi [4]. The glasses employed had compositions of $(33-X)(R_2O) \cdot XAl_2O_3 \cdot 67SiO_2$ where R_2O stands for Na_2O, K_2O or ($0.5Na_2O \cdot 0.5K_2O$) and X = 5.5, 9.4 and 16.5 mol% . Various glasses were produced by keeping the silica content fixed at 67 mol% and varying the mole ratio of Al_2O_3/R_2O from 0.2, 0.4 to 1 in an effort to reduce the non-bridging oxygen content systematically. The nominal compositions of the glass used in the present experiment are listed in Table 1, along with the glass transition temperatures for selected glass compositions which have been obtained from a handbook [17]. Although the glass transition temperatures for other glasses were not available, it is known, in general, that the glass transition temperatures of mixed alkali glasses are lower than the corresponding single alkali glasses.

A mixture of reagent grade SiO_2, Al_2O_3, Na_2CO_3, and K_2CO_3 was prepared such that approximately 100 grams of glass would be obtained after melting. The prepared mixture of powder was dried for approximately 12 h at 200 °C prior to melting. The glasses with Al_2O_3/R_2O of 0.2 and 0.4 were melted in a 100% Pt crucible at 1650 °C and the glass with Al_2O_3/R_2O of 1 was melted in a crucible consisting of 90% Pt/10% Rh at 1750 °C. All melts were left to fine until all bubbles had disappeared. Glasses, except the highest alumina containing glass, were poured on a metal plate and transferred to an annealing furnace set at 500 °C. Due to the high viscosity of the highest alumina containing glass, the bottom of the crucible containing the melt was quenched in cold water to separate the glass from the crucible, and then the glass was immediately moved into a pre-heated furnace at 500 °C where it was left to anneal for 2 days.

The resulting glass melts were cut into 12 mm × 12 mm square samples with thickness 10 mm using a diamond bladed saw. The samples were then sliced down to approximately 0.5 mm thicknesses to obtain the final dimensions of 12 mm × 12 mm × 0.5 mm. The final samples were heat-treated in a furnace at 500 °C for twelve hours and then quenched on a cold metal plate to fix the fictive temperature at approximately at 500 °C.

The densities of the glass samples were measured at room temperature using the Archimedes method with water as the liquid medium. From the obtained density values of the glasses, the molar volumes were determined for each glass. These measured densities and obtained molar volumes are tabulated in Table 1. The molar volume was found to change linearly with the alkali mole fraction, e.g. $K_2O/(Na_2O + K_2O)$ for all of the glass systems, consistent with what has been reported in the literature [2]. Using this linear relationship, a density vs. composition relationship was established. This density-composition relationship was used to estimate the final glass composition for each glass after the complete ion-exchange.

Variations of molar volumes of single alkali Na_2O glass and K_2O glass with alumina additions are shown in Fig. 1. It is interesting to note that as the ratio of Al_2O_3/R_2O increased, the molar volume of the single alkali potassium glass remained nearly constant, while the volume of the sodium glass steadily increased. In this paper, unlike the previous paper [3], ΔV, will be defined as the molar volume mismatch as defined below, instead of the absolute difference in molar volume. The volume mismatch is defined as:

$$\Delta V = \frac{V_1 - V_2}{V_{12}} \tag{1}$$

where V_1 is the molar volume of the single alkali glass with a larger volume, V_2 is the molar volume of the single alkali glass with a smaller volume, and V_{12} is the mean of the two. This parameter has been used previously by Davies and Navrotsky [18] who found a good correlation between the positive enthalpy of mixing of solid solution and this volume of mismatch, or the difference of the volumes of the corresponding single components normalized by the volume of one component. It can be seen the molar volume mismatch, ΔV, of Na_2O glass and K_2O glass decreases with increasing alumina content as is shown in Table 2.

In the ion-exchange experiments, glass samples were treated in molten salt mixtures of KNO_3 and $NaNO_3$ with varying fraction of an alkali species for 6 h at a time at 500 °C. During each treatment, the

Table 1
Compositions and selected properties of glasses prepared.

Composition	Al_2O_3/R_2O	Density ± .0002 (g/cm^3)	Molar volume (cm^3/mol)	T_g (°C)
$27.5\ Na_2O \cdot 5.5\ Al_2O_3 \cdot 67\ SiO_2$	0.2	2.4604	25.57	490
$27.5\ (0.5Na_2O + 0.5K_2O) \cdot 5.5\ Al_2O_3 \cdot 67\ SiO_2$	0.2	2.4446	27.55	
$27.5\ K_2O \cdot 5.5\ Al_2O_3 \cdot 67\ SiO_2$	0.2	2.4304	29.53	
$23.6\ Na_2O \cdot 9.4\ Al_2O_3 \cdot 67\ SiO_2$	0.4	2.4415	26.41	500
$23.6\ (0.5Na_2O + 0.5K_2O) \cdot 9.4\ Al_2O3 \cdot 67\ SiO_2$	0.4	2.4443	27.93	
$23.6\ K_2O \cdot 9.4\ Al_2O_3 \cdot 67\ SiO_2$	0.4	2.4469	29.45	
$16.5\ Na_2O \cdot 16.5\ Al_2O_3 \cdot 67\ SiO_2$	1	2.3449	28.70	525
$16.5\ (0.5\ Na_2O + 0.5K_2O) \cdot 16.5\ Al_2O_3 \cdot 67\ SiO_2$	1	2.4124	29.00	
$16.5\ K_2O \cdot 16.5\ Al_2O_3 \cdot 67\ SiO_2$	1	2.4777	29.31	