Mutual diffusivity, network dilation, and salt bath poisoning effects in ion-exchanged glass

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ABSTRACT

Chemically strengthened glass produced via the ion exchange process has found many interesting applications due to its high strength and damage resistance. It is known that salt bath poisoning has a strong effect on mutual diffusivity during the ion exchange process. Salt bath poisoning occurs when cations previously in the glass contaminate the molten bath nominally consisting of a larger substituting cation. In this work, we introduce a simple two-level model describing the impact of salt bath poisoning on the mutual diffusion coefficient. The model is compared to experimentally measured values of mutual diffusivity over a wide range of salt bath poisoning and glass composition. The model is shown to agree well with the experimental data. We also quantify the dependence of the activation energy for mutual diffusivity on the initial concentration of the substituting cation in the base glass composition. Finally, we address the issue of network dilation during ion exchange, showing that the magnitude of the "network dilation anomaly" is lower for aluminosilicate glasses as compared to soda lime float glasses, enabling them to achieve closer to their ideal values of strength.

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1. Introduction

Ion exchange takes place when a glass containing mobile cations comes in contact with a molten salt bath containing dissimilar cations [1]. When smaller cations in the glass are replaced by larger substituting cations from the molten salt bath, a compressive stress is generated at the glass surface. This compressive stress can attain values up to approximately 1 GPa. As a result, it becomes significantly more difficult for cracks to form and propagate at the surface of the glass.

The ion exchange process for glass strengthening was first proposed by Kistler [2] and by Acloque and Tochon [3] in 1962 [4]. Since then, ion exchange has become widely utilized for its ability to generate higher compressive stresses compared to other strengthening techniques such as thermal tempering [5–7]. Ion exchange also has the unique ability of being able to strengthen glasses with complex geometries [7–11]. The refractive index change induced through ion exchange is also useful in the manufacture of gradient index lenses and waveguides [12].

Chemical strengthening via ion exchange, however, can be compromised by salt bath "poisoning," which occurs when the molten salt bath is contaminated with some concentration of the smaller cations already present in the glass. Such contamination can occur as a result of the long immersion time of the glass in the salt bath, or if the size of the salt bath is small compared to that of the glass samples.

It is known that salt bath poisoning significantly reduces the efficacy of the chemical strengthening process by lowering the thermodynamic driving force for ion exchange [5]. It is therefore necessary for the bath to be replaced with fresh salt when contamination reaches an unacceptable level [5].

Despite the importance of salt bath poisoning in industrial practices, there is currently no model that describes mutual diffusivity as a function of salt bath poisoning. Previous models have focused on the thermodynamic rather than kinetic aspects of salt bath composition effects. For example, Araujo et al. [12] have evaluated the thermodynamic energies of interaction for distinct ions based on sigmoidal equilibrium graphs of the glass and molten salt. Araujo [1,13] has also studied the thermodynamic driving force of ion exchange and created a one-dimensional model that describes its boundary conditions. Houde-Walter and coworkers [14–17] subsequently extended that model to three dimensions.

In this paper, we introduce a model for the effect of salt bath poisoning on the kinetics of mutual diffusivity and show good agreement with experimental data obtained for a series of aluminosilicate and soda lime float glasses. We also determine the chemical dependence of the activation barrier for mutual diffusivity. Furthermore, we investigate the composition dependence of the linear network dilation coefficient (LNDC), which defines the amount of linear strain in the glass per unit of ions exchanged. Of particular interest is the so-called "network dilation anomaly," which refers to the discrepancy between calculated values of the LNDC for as-melted versus ion-exchanged glasses. This anomaly will be discussed further in Section 2.2. While both aluminosilicate and soda lime glasses exhibit a network dilation anomaly, the

effect is much smaller in the aluminosilicate glasses, enabling them to reach closer to their ideal values of compressive stress.

2. Theory

2.1. Mutual diffusivity model

The mutual diffusion coefficient, D, is a parameter that describes how quickly different types of cations exchange places by diffusive hopping as a result of a concentration gradient between the glass and salt bath [4]. This is the principal mechanism for ion exchange. For the purposes of the present discussion, let us assume that the ion exchange process consists of sodium ions in the glass being exchanged for larger potassium ions from the salt bath. Our model considers the mutual diffusivity to be comprised of a mixing of end member values:

$$D(f_{Na}) = p_K D(0) + p_{Na} D(1). \tag{1.1}$$

Here, $D(0)$ is the mutual diffusivity in the limit of zero bath poisoning ($f_{Na} = 0$, where f_{Na} denotes the mole fraction of Na$^+$ in the salt bath) and $D(1)$ is the mutual diffusivity in the limit of a completely poisoned salt bath ($f_{Na} = 1$). The parameters p_K and p_{Na} are the selection probabilities for K$^+$ and Na$^+$ ions, respectively. Please note that

$$f_K + f_{Na} = 1 \tag{1.2}$$

since we assume that there are no other cations in the salt bath. The mutual diffusivity, D, has an Arrhenius temperature dependence for all temperatures of interest, i.e., the range of temperatures above the melting point of the salt and below the strain point of the glass.

The model assumes a fixed number of alkali sites occupied by either potassium or sodium ions. For the purposes of this work, we assume that the salt bath provides a large reservoir of ions such that composition of the bath is unchanged during the course of a single ion exchange experiment (i.e., we assume a semi-infinite salt bath). However, a time-dependent bath composition could also be introduced by considering the finite size of the salt bath. This is especially pertinent for when the volume of the salt bath is small compared to the size of the glass, or for especially long ion exchange treatments without replacement of the salt.

The selection probabilities are calculated via a simple two-level (i.e., binary) statistical mechanical model describing the diffusive hopping of either the sodium or potassium ions. To do this, it is assumed that the glass reaches its equilibrium surface concentration in a short period of time compared to the overall ion exchange duration [12]. This equilibrium is defined as the point when the electrochemical potentials of the cations are equal in the two phases [18]. The two-level model is used to randomly select either a sodium or potassium ion for diffusive hopping. The selection probability of potassium, p_K, is determined by the product of an entropic factor (the mole fraction, f_K) and a Boltzmann factor divided by the partition function as:

$$p_K = \frac{f_K \exp\left(-\frac{\Delta H}{kT}\right)}{f_{Na} + f_K \exp\left(-\frac{\Delta H}{kT}\right)}. \tag{1.3}$$

Here, k is the Boltzmann constant, T is the absolute temperature under which the ion exchange is conducted, and ΔH is the difference between the activation barriers for potassium and sodium hopping. Since potassium ions have a greater activation barrier for diffusive

hopping, ΔH should have a positive value. The selection probability of sodium can be calculated similarly by:

$$p_{Na} = \frac{f_{Na}}{f_{Na} + f_K \exp\left(-\frac{\Delta H}{kT}\right)}. \tag{1.4}$$

By combining Eqs. (1.1)–(1.4), we obtain

$$D = \frac{\left[(1-f_{Na})D(0)\exp\left(-\frac{\Delta H}{kT}\right) + f_{Na}D(1)\right]}{f_{Na} + (1-f_{Na})\exp\left(-\frac{\Delta H}{kT}\right)}, \tag{1.5}$$

which can also be written as

$$D = [D(0)-D(1)]\frac{\left[(1-f_{Na})\exp\left(-\frac{\Delta H}{kT}\right)\right]}{f_{Na} + (1-f_{Na})\exp\left(-\frac{\Delta H}{kT}\right)} + D(1). \tag{1.6}$$

In all, this model introduces three parameters: $D(0)$, $D(1)$, and ΔH, which can be fitted to measured values of diffusivity as a function of salt bath contamination. These parameters are discussed in more detail in Section 4.

The mutual diffusion process changes the glass structure as the invading ions from the salt bath penetrate deeper into the glass [7,8]. These structural modifications include a change in the cation coordination number and number of non-bridging oxygens around the ion site [18]. Quaranta et al. [18] argue that the ion exchange equations should also account for the dependence of diffusion parameters on the concentration profile of the alkali species in the glass. This phenomenon has been most thoroughly studied in the Ag$^+$–Na$^+$ [19–21] and Cu$^+$–Na$^+$ [22,23] systems because of their applications as optical waveguides. The values of mutual diffusivity in the current work should be interpreted as average values throughout the depth of the glass, assuming Fickian diffusion such that the concentration profile follows a complementary error function.

2.2. Linear network dilation coefficient

The linear network dilation coefficient, B, is also studied in this work. This coefficient was first suggested by Richmond et al. [24] and defines the amount of linear strain that the glass undergoes per unit of ions exchanged. There are two approaches for obtaining the value of B. First, assuming negligible stress relaxation, the compressive stress $\sigma(z)$ at penetration depth z can be calculated as:

$$\sigma(z) = -\frac{BE}{1-v}\left[C(z)-C_{avg}\right]. \tag{2.1}$$

Here, E is Young's modulus, v is Poisson's ratio, $C(z)$ is the local concentration of the substituting cation in the glass at depth z, and C_{avg} is the average concentration of the substituting cations in the glass. The values of B may also be calculated through

$$B = \frac{1}{3V}\frac{\partial V}{\partial C} = \frac{1}{3}\frac{\partial \ln V}{\partial C} \tag{2.2}$$

where V is the molar volume of the as-melted glass with different concentrations of potassium. Fig. 1 plots the measured values of molar volume for the two series of glasses used in this study.

The so-called "network dilation anomaly" arises from a discrepancy between values of B obtained through Eq. (2.1) using ion-exchanged glass and through Eq. (2.2) based on as-melted (unexchanged) glasses. It has been found that the network dilation coefficient from Eq. (2.2) is generally a factor of 2–4 larger than that from Eq. (2.1) [4–7,25]. This is