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## LETTER TO THE EDITOR

# Diffusion with memory: a model for mixed alkali effects in vitreous ionic conductors

A Bunde†, M D Ingram‡, P Maass† and K L Ngai§

† Institut für Theoretische Physik, Universität Hamburg, Jungiusstrasse 9, D-2000 Hamburg 36, Federal Republic of Germany

‡ Department of Chemistry, University of Aberdeen, Old Aberdeen, UK

§ Naval Research Laboratory, Washington, DC 20375, USA

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**Abstract.** We present a novel theory of the mixed alkali effect which focuses on the fact that each alkali prefers and maintains its own distinct characteristic environment in the mixed glass. This leads to mismatch between cations and sites recently occupied by unlike cations, and the existence of a memory effect which strongly influences the process of ion migration. This view of glass is consistent with both EXAFS and infrared measurements, and computer simulations reproduce the essential features of the mixed alkali effect including the mobility crossover and the conductivity minimum.

The mixed alkali effect (MAE) is one of the outstanding unresolved problems in the physics of glassy ionic conductors. In mixed Li/K silicate glasses, for example, the ionic conductivity goes through a deep minimum as the ratio of Li to K is varied. The effect becomes more pronounced as the temperature is lowered and conductivities of mixed glasses can be some four powers of ten lower than either of the single alkali glasses. Furthermore, there are strong effects on the diffusion coefficients of the individual cations: when one alkali ion is replaced by another, the diffusion coefficient of the former always decreases. There is an intersection of the diffusion coefficient curves of the two alkalis at some particular alkali ratio where both cations have the same mobility. This composition is close to the minimum in the ionic conductivity.

This pattern of behaviour is widespread (for references see [1, 2]). It occurs in *all* glasses of general formula  $xX_2O-(1-x)Y_2O-(SiO_2 \text{ or } B_2O_3 \text{ or } GeO_2)$  where  $X_2O$  and  $Y_2O$  are different network modifying alkali oxides, in related sulphide systems, and in crystalline  $\beta$ -gallates and  $\beta$ -aluminas. Mixed 'alkali' effects are also seen in glasses containing protons,  $Ag^+$  and  $Tl^+$  ions, and there is a corresponding effect in mixed  $F^-/Cl^-$  glasses where the anions are the principal current carriers. Despite increased interest in the effect in recent years, still no theory fully accounts for all features of the MAE and there is considerable disagreement concerning the origin of the effect [1-3].

Recently, Greaves *et al* [4] have examined the alkali cation environments in single and mixed alkali silicate glasses ( $K_2Si_2O_5$ ,  $CsSi_2O_5$  and  $KCsSi_2O_5$ ) by EXAFS measurements. They found that each alkali maintains approximately its own characteristic environment in the mixed glass: the K—O bond length is 2.81 Å in  $K_2Si_2O_5$  and 2.71 Å in  $KCsSi_2O_5$ , and the Cs—O bond length is 3.12 Å in  $Cs_2Si_2O_5$  and 3.09 Å in  $KCsSi_2O_5$ . The results of Greaves *et al* are in accord with earlier conclusions based on far infrared spectroscopy [5], that the local environment of any cation in glass is largely unaffected

by the addition of a second cation. In this way, the distinction between the two types of cationic environments can lead to 'mismatch' effects (between ions and sites) when a particular cation tries to diffuse through a mixed cation glass.

In this letter we construct a microscopic model of alkali diffusion in mixed alkali systems which is based on the aspect of mismatch between dissimilar cation environments. We distinguish between two types of cations,  $A$  and  $B$ , and two types of vacancies,  $\bar{A}$  and  $\bar{B}$ . An  $\bar{A}$  site is a vacant site that was latterly occupied by an  $A$  ion, and a  $\bar{B}$  site is a vacant site latterly occupied by a  $B$  ion. We assume that both types of sites keep their identity for a certain time interval. If an  $\bar{A}$  or  $\bar{B}$  site is empty for more than  $\tau_A$  or  $\tau_B$  time steps it relaxes to some type of interstitial site which is neither adjusted to an  $A$  ion nor a  $B$  ion. For simplicity (and in order to reduce the number of parameters as much as possible) we shall focus here on the case of a large concentration of mobile ions, where the probability that a site has not been visited for a long time is small and the influence of finite relaxation times  $\tau_A$  and  $\tau_B$  can be neglected. For a discussion of the effect of finite relaxation times with regard to diffusion in single ionic glasses we refer to [6].

In the microscopic model we define the jump probabilities of cations  $A$  and  $B$  to vacant nearest-neighbour sites  $\bar{A}$  and  $\bar{B}$  by  $W_{A\bar{A}} = \nu_{A\bar{A}} \exp(-E_{A\bar{A}}/k_B T)$ ,  $W_{A\bar{B}} = \nu_{A\bar{B}} \exp(-E_{A\bar{B}}/k_B T)$ ,  $W_{B\bar{A}} = \nu_{B\bar{A}} \exp(-E_{B\bar{A}}/k_B T)$  and  $W_{B\bar{B}} = \nu_{B\bar{B}} \exp(-E_{B\bar{B}}/k_B T)$ . We assume that the environment of the vacant site  $\bar{A}$  must distort in order to accommodate the arrival of alkali  $B$ , and the environment of  $\bar{B}$  must distort in order to accommodate the arrival of alkali  $A$ . Since the lattice distortion requires appropriate elastic energies  $\Delta E_{A\bar{B}}$  and  $\Delta E_{B\bar{A}}$ , we can write

$$E_{A\bar{B}} = E_{A\bar{A}} + \Delta E_{A\bar{B}} \quad E_{B\bar{A}} = E_{B\bar{B}} + \Delta E_{B\bar{A}}. \quad (1)$$

Energy of distortion of the environment is always positive, hence both  $\Delta E_{A\bar{B}}$  and  $\Delta E_{B\bar{A}}$  are positive. This implies

$$W_{A\bar{B}} < W_{A\bar{A}} \quad W_{B\bar{A}} < W_{B\bar{B}}. \quad (2)$$

We have performed computer simulations to explore the consequences of the model. For simplicity we have assumed that the ion migration is restricted to two dimensions. This assumption is consistent with ideas of structural granularity [2, 7] in glass, and the related suggestion that conduction pathways are located within a *connective tissue* which surrounds less conductive microdomains or clusters. To some extent, this resembles the situation in crystalline  $\beta$ -alumina, where the cations move within two-dimensional layers.

In the simulation, first the sites of a square lattice (usually of size  $150 \times 150$ ) are randomly occupied by cations  $A$  with concentration  $c_A$  and cations  $B$  with concentration  $c_B$ . The total of  $N$  ions are labelled so that  $A$  and  $B$  ions are distinguishable. Next, an ion is chosen randomly, and a nearest-neighbouring site is also chosen to which the ion attempts to jump. If the neighbouring site is occupied by another ion, the jump is rejected. If the neighbouring site is empty, the ion jumps to it with a probability that can be either  $W_{A\bar{A}}$ ,  $W_{A\bar{B}}$ ,  $W_{B\bar{B}}$  or  $W_{B\bar{A}}$  depending on the chosen ion and the history of that neighbouring empty site. The transition probabilities of  $A$  or  $B$  ions to unspecified sites (which occur only at the beginning of the simulation) are chosen as  $W_{A\bar{A}}$  or  $W_{B\bar{B}}$ , respectively. After the trial, time is incremented by  $1/N$ , regardless of whether the ion has jumped. Next a new particle is chosen and the process is repeated again and again, until thermal equilibrium is reached and then the relevant quantities are determined.

To reduce the number of parameters involved, we have chosen all prefactors the same,  $\nu_{A\bar{A}} = \nu_{B\bar{B}} = \nu_{A\bar{B}} = \nu_{B\bar{A}} = \nu$ , and considered a symmetric situation where  $E_{A\bar{A}} = E_{B\bar{B}}$  and  $\Delta E_{A\bar{B}} = \Delta E_{B\bar{A}} = k_B T_0$ . Since now the factor  $\nu \exp(-E_{A\bar{A}}/k_B T)$  occurs in all four transition probabilities, it only modifies the overall time scale and can be set equal to one without loss of generality. The calculations are made at different temperatures  $T_0/T$  and different mixed alkali concentrations  $x = c_A/(c_A + c_B)$ . We take  $c_A + c_B = 0.65$ , so 35% of the sites are unoccupied.

Figure 1 shows the structural pathways in the system occurring at a certain instant of time at temperature  $T_0/T = 2 \ln(10)$ , i.e. when  $\bar{W}_{A\bar{B}} = \bar{W}_{B\bar{A}}$  is 100 times less than  $\bar{W}_{A\bar{A}} = \bar{W}_{B\bar{B}}$ . The structural paths for the A ions (A paths) consist of those sites  $\bar{A}$  which are either occupied by an A ion or have been latterly occupied by an A ion. In the figure, the A paths are marked by squares, the rest of the lattice represents the B paths. At small A concentration ( $x = 0.2$ , figure 1(a)), there exists an 'infinite' B path connecting opposite edges of the lattice, which surrounds small clusters of  $\bar{A}$  sites. By symmetry, the set of configurations at  $x = 0.2$  and  $x = 0.8$  are identical if A and B sites are mutually interchanged, so the picture also illustrates the case  $x = 0.8$  where now the marked sites represent the B paths. At identical A and B concentrations ( $x = 0.5$ , figure 1(b)), only finite pathways exist for both types of ions.

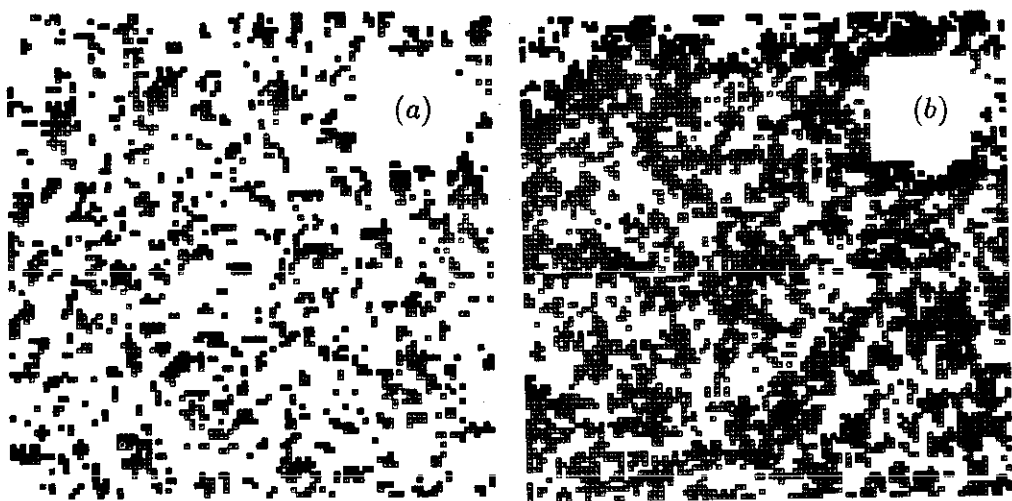


Figure 1. Fluctuating A paths ( $\square$ ) and B paths for the mixed alkali concentrations (a)  $x = 0.2$  and (b)  $x = 0.5$ , for  $T_0/T = 2 \ln(10)$ .

Hence, by the mismatch between dissimilar cations an element of percolation is introduced. The structures, however, are highly correlated and differ considerably from ordinary percolation [8, 9]. This is shown more quantitatively in figure 2 where the pair correlation functions  $g_{\bar{A}\bar{A}}(r)$  and  $g_{\bar{A}\bar{B}}(r)$  are shown for the same parameters as in figure 1,  $T_0/T = 2 \ln(10)$  and  $x = 0.2$  (figure 2(a)) and 0.5 (figure 2(b)). The pair correlation functions are defined as usual; for example,  $g_{\bar{A}\bar{B}}(r)$  is the probability to find a  $\bar{B}$  site at distance  $r$  from a given  $\bar{A}$  site, divided by the concentration of  $\bar{B}$  sites. The correlations have maximum range at  $x = 0.5$  (where the minimum in the total conductivity appears). For increasing temperatures, the correlations decrease. For  $T_0/T \rightarrow 0$ , all pair correlations tend to one for  $r > 0$ , as in the case of ordinary percolation systems. We like to note that the clustering of like cations is a phenomenon whose

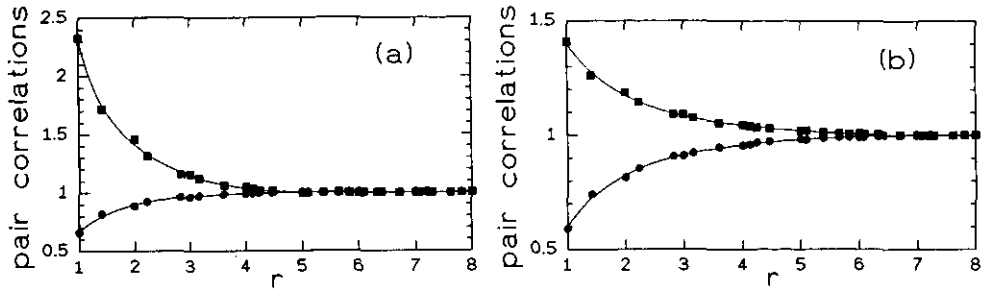


Figure 2. Pair correlation functions  $g_{A\bar{A}}$  (■) and  $g_{A\bar{B}}$  (●) for (a)  $x=0.2$  and (b)  $x=0.5$  as a function of distance  $r$ , for  $T_0/T = 2 \ln(10)$ .

existence has already been substantiated from x-ray diffraction studies of Na/Tl borate glasses [10].

Next we consider the transport quantities. By inspection of figure 1 we can expect different behaviour at  $x=0.2$ , 0.8 and 0.5. At  $x=0.2$  (or 0.8) the  $B$  ions (or  $A$  ions) can stay on their pathways, and transport is dominated by the large transition probabilities  $W_{BB} = W_{A\bar{A}}$ . In contrast at  $x=0.5$ , an ion has to leave its pathway to move from one end of the system to the other, and transport is governed by the small transition probabilities  $W_{AB} = W_{B\bar{A}}$ . This changeover from single-cation to mixed cationic conduction is well authenticated by transport measurements [11] and it is important that it emerges quite naturally from the theoretical model (compare [12] for discussion of this topic).

Figure 3 shows the conductivity obtained from the current response to an external sinusoidal field (for a description of the technique, we refer to [14]), as a function of mixed alkali concentration  $x$  for (a) fixed (small) frequency  $\omega = 0.01$  and four temperatures,  $T_0/T = \ln(10)$ ,  $\frac{4}{3} \ln(10)$ ,  $\frac{3}{2} \ln(10)$ ,  $2 \ln(10)$ , and (b) for fixed temperature  $T_0/T = 2 \ln(10)$  and three frequencies,  $\omega = 0.1$ , 0.01 and 0.002. The curves show a broad minimum at  $x=0.5$  which is deeper at lower temperatures and lower frequencies, in apparently good agreement with experiment [14]. The same holds for larger  $T_0$  when the mismatch between the two cations is stronger and indeed a stronger effect, for example, in Li/Cs than in the Na/K system, has been observed experimentally [1, 2, 11]. However, we are cautious about relating the mismatch energy directly to the size of the ions, as would be the case if it were simply an elastic strain energy along the lines

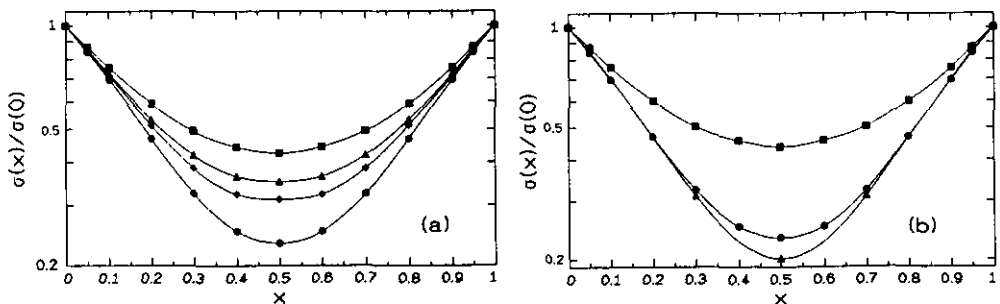


Figure 3. Plot of the normalized real part of the ac-conductivity  $\sigma(x)/\sigma(0)$  as a function of  $x$  at (a) fixed frequency  $\omega = 0.01$  and four temperatures  $T_0/T = \ln(10)$  (■),  $\frac{4}{3} \ln(10)$  (▲),  $\frac{3}{2} \ln(10)$  (◆) and  $2 \ln(10)$  (●), and (b) fixed temperature  $T_0/T = 2 \ln(10)$  and three frequencies  $\omega = 0.1$  (■), 0.01 (●) and  $\omega = 0.002$  (▲).

of the classical Anderson-Stuart theory [15]. The existence of a significant MAE [16] in Na/Ag glasses (where the molar volumes of the cations are very similar) suggests that 'chemical' mismatches are just as important; the memory effect more probably involves limited bond rearrangements within the glass framework.

Figure 4 shows, for  $T_0/T = \ln(10)$  and  $T_0/T = 2 \ln(10)$ , the diffusion coefficients  $D_A(x)$  and  $D_B(x)$  of ions A and B respectively. By substituting ions of one type by dissimilar ions of the second type, the diffusion coefficient of the remaining primary ions always decreases. This effect becomes more pronounced at smaller temperatures (or larger  $T_0$ ), in agreement with the experimental situation. For  $T \rightarrow 0$  the A and B paths freeze in, and we expect that the ratios  $D_A(x)/D_A(1)$  and  $D_B(x)/D_B(0)$  tend to zero in a certain concentration range around  $x = 0.5$ , where no 'infinite' A or B path exists.

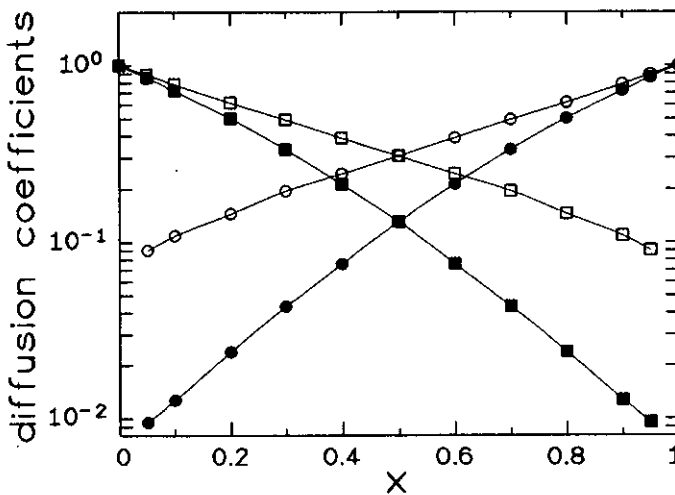


Figure 4. Normalized diffusion coefficients  $D_A(x)/D_A(1)$  and  $D_B(x)/D_B(0)$  of cations A and B as a function of the mixed alkali concentration  $x = c_A/(c_A + c_B)$  for temperatures  $T_0/T = \ln(10)$  (○, □) and  $T_0/T = 2 \ln(10)$  (●, ■). The open and filled circles refer to the A ions, the open and filled squares to the B ions.

In summary, we have presented a new model for ionic transport in mixed alkali systems that is based on the mismatch between dissimilar cations. The mismatch leads naturally to memory effects and to the appearance of fluctuating A and B paths for the ions. At intermediate mixed alkali concentrations both pathways do not percolate through the system, and this leads to the pronounced minimum in the conductivity and to the anomalous behaviour of the diffusion coefficients. This effect is not specific for two dimensions, but (as preliminary numerical calculations show) occurs also in three dimensions where a certain fraction of sites are reluctant host sites for the mobile ions.

To bring out clearly the structural origin of the mixed alkali effect, we have chosen the simplest type of parameters. In a realistic system, the parameters can be asymmetric and the ions interact mutually. But we can argue that this does not change the effect qualitatively. Asymmetric parameters lead to asymmetric curves of the diffusion coefficients and the conductivity. Long-range interactions [17] will have some effect

on the width of the minimum, and will change the internal structure of the pathways as well as the conductivity relaxation but the overall picture will be the same.

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