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A Molecular Dynamics Investigation of the Structures and Mixed Alkali Effect in Sulfate Glasses*

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

A molecular dynamics stimulation of alkali sulfate–zinc sulfate melts and glasses is presented. Oxygen coordinations of Zn^{2+}, Na^{+}, and K^{+} cations have been found to be nearly six, eight, and twelve respectively. The radial distribution function has been calculated and compared with the same reported from experimental X-ray diffraction work. Several important aspects of a modified random close packing model described earlier to account for the behavior of sulfate glasses have been confirmed by the present molecular dynamics simulation. Diffusion coefficients of various ions have been evaluated from mean squared displacement data and occurrence of the mixed alkali effect has been noted. A surprising spatial correlation of dissimilar alkali ions has been observed and it is suggested that it provides support for a structural origin of mixed alkali effect in ionic glasses. © 1993 Academic Press, Inc.

Introduction

It has been known for a long time that glasses can be obtained by quenching melts of binary salt systems such as calcium nitrate–alkali nitrate and zinc sulfate–alkali sulfate (*1, 2*). These glasses generally possess low glass transition temperatures and have therefore been of great interest as model systems for studying various properties of glasses. A fascinating aspect of these glasses is that the constituents of the glass structure are simple cations and small discrete oxyanions. An ensemble of such small discrete entities which interact dominantly through coulombic forces should be expected to crystallize readily into one or more phases depending upon the nature of the constituents. However, in some regions of composition, melts of such binary sulfates and nitrates can be quenched easily into glasses even with moderate rates of quenching (approximately 10^3 K/sec). It is interesting to investigate the nature of the local and long range structures of such glasses.

A number of experimental studies have been conducted on zinc sulfate–alkali sulfate glasses in this laboratory, particularly X-ray diffraction and electronic spectra of probe divalent ions in order to investigate the structures (*3–6*). Similar investigations have been made on glasses containing two different alkali ions (*7*). Based on a number of such studies a modified random close packing (rcp) model of zinc sulfate–alkali sulfate glasses has been proposed and the main features of the model will be discussed later.

Several physical properties of the sulfate glasses have been found to be consistent with the modified rcp model. Configurational entropies of the glasses have been calculated on the basis of the above model

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and the glass formation region has been shown to be associated with very high configurational entropies (*2*).

Since the potentials of interaction in this model are entirely coulombic, except within the sulfate ions themselves, it is rather appropriate to examine important structural and dynamical aspects of sulfate glasses using molecular dynamics (MD) simulation. In this paper we focus attention on structures of select binary and ternary sulfate glasses and highlight the results of MD simulation which has provided very strong support for the structural model proposed earlier for these glasses. In particular we discuss the coordinations of all the cations and the dynamics of various species present in the glass in the background of the phenomenon of mixed alkali effect observed experimentally in these glasses.

Details of Computer Simulation

The molecular dynamics simulation was performed on N particles in a microcanonical (NEV) ensemble. The system consists of discrete ions of zinc, potassium, and sodium and rigid tetrahedral sulfate (SO_4) groups. The site–site interaction potential employed was of the Born–Meyer–Huggins (BMH) form:

$$U_{ij} = Z_i Z_j e^2/r_{ij}\,\mathrm{erf}_c(r_{ij}/\eta L) + A_{ij}\exp\{(\sigma_{ij} - r_{ij})/\rho\}, \quad (1)$$

where $A_{ij} = b_{ij}[1 + Z_i/n_i + Z_j/n_j]\exp(\sigma_{ij}/\rho_{ij})$.

We have ignored the van der Waals and polarization energy contributions. η_i denote the number of valence shell electrons. The charges on sulfur and oxygen were those used by Impey and co-workers in their work on crystalline Li_2SO_4 (*8*). The coulombic interactions were evaluated using the Ewald sum method. Periodic boundary conditions were applied to simulate an infinite system. The various parameters involved in the potential are given in Table I. The density and the size of the computational cell are given in Table II. The S–O distance in the tetrahedron was maintained to be 1.48 Å, the same as in crystalline $ZnSO_4$. The hard sphere diameter of oxygen was chosen to be 1.22 Å to reproduce correct Zn–O distances. Orientation of (SO_4) units were specified by quaternions (q_0,q_1,q_2,q_3) (*9*). Each time step consisted of the translation of the centers of mass and the rotation of the (SO_4) groups. The equations of motion were integrated using the fifth order predictor–corrector method with a time step of 1×10^{-15} sec.

The runs were started from an initially random configuration of the centers of masses inside a cubic box of a size appropriate to the density of the system. The initial quaternion parameters of all (SO_4) groups were taken as (1,0,0,0). Samples were equilibrated for around 10,000 time steps (10 psec) at 6000 K and then quenched to 3000 K. They were further equilibrated at 3000 K and 700 K for an equal number of time steps and later a final quench to 300 K was performed. Equilibration runs at 300 K were typically for over 10 psec. Velocity rescaling was adopted during the equilibration to keep the system at the specified temperatures. The total energy of the system was constant to five parts in 10^4.

The results discussed here were obtained after sufficient averaging. Static properties like the pair distribution functions were averaged over a period of 20 psec sufficiently after equilibration. Positions and velocities of individual species in the system were stored every 10 fsec for over 20 psec. Dynamical properties such as mean squared displacements and the velocity autocorrelation functions were obtained from the stored data and were calculated for nearly 10 psec. The time step, total times for equilibration, time for averaging, and other computational parameters are fully comparable with those of similar studies in the literature (*10, 11*).

Results and Discussion

We have simulated several compositions of sulfate glasses by the MD technique. But for the purpose of this article, we discuss

TABLE I

POTENTIAL PARAMETERS USED IN EQUATION (1)

	Zn	K	Na	S	O
Z_i	+2.0	+1.0	+1.0	+1.2	−0.8
σ (Å)	2.5	2.926	2.34	2.04	2.44

Note. $\eta = 0.1786$, $\rho = 0.29$ Å, and $b_{ij} = b = 0.338 \times 10^{-19}$ J.

the simulation work related to three compositions C1, C3, and MIX which correspond to $(Na_2SO_4 : K_2SO_4 : ZnSO_4) : : (0,50,50)$, (50,0,50), and (25,25,50) respectively (all in molar percentages). Data on one other composition C2 which is a binary $75ZnSO_4$–$25K_2SO_4$ glass is included in order to make comparisons between radial distribution functions obtained from experimental X-ray diffraction studies and from MD simulation. It will be seen later that when the melts are quenched to 300 K, the mean squared displacements of the ions are reduced to very low values (to $<10^{-8}$ cm^2/sec) and hence we conclude that glassy phases have been attained. Further, experimental glass transition temperatures are well above 450 K for all sulfate glasses in this system. Hence we did not perform any further tests to ascertain incidence of a glass transition. Attention is confined in this paper to three specific aspects of sulfate glasses where comparisons could be made directly between MD simulation results and earlier work from this laboratory: (1) Local structures around the three cations, namely Na, K, and Zn. (2) Long range structures in the form of radial distribution functions for the three compositions. (3) Diffusion coefficients of alkali ions in the simulated glasses.

Local Structures

The pair distribution functions (PDFs) for Zn–O, K–O, and Na–O are shown in Figs. 1a, 1b, and 1c, respectively. It is evident from the figures that the distance of the first neighbor shell is sharp while the distance to higher neighbors are broad. Considering the cut-off distances indicated by arrows, the number of first neighbor oxygens for the three cations in the three glass compositions are summarized in Table III. In Fig. 2, the PDFs (M–S, where M stands for Zn, K, and Na) are shown and the relevant data is again summarized in Table IV. We have suggested earlier (*1*) that alkali sulfate–zinc sulfate glasses which are typically highly ionic can be modeled using random close packing concepts. Central to this model is the recognition of the fact that SO_4^{2-} ions have a rotational envelope of a sphere and are referred

TABLE II

DENSITIES (*8*), SIZE OF THE SIMULATION CELL, AND THE COMPOSITIONS STUDIED

	C1	C2	C3	MIX
Density (g/cm^2)	2.8	3.08	3.02	2.901
Box length (Å)	17.054	16.650	16.098	16.598
N	325	325	325	325
Component		Composition (mole%)		
Na_2SO_4	0	0	50	25
K_2SO_4	50	25	0	25
$ZnSO_4$	50	75	50	50

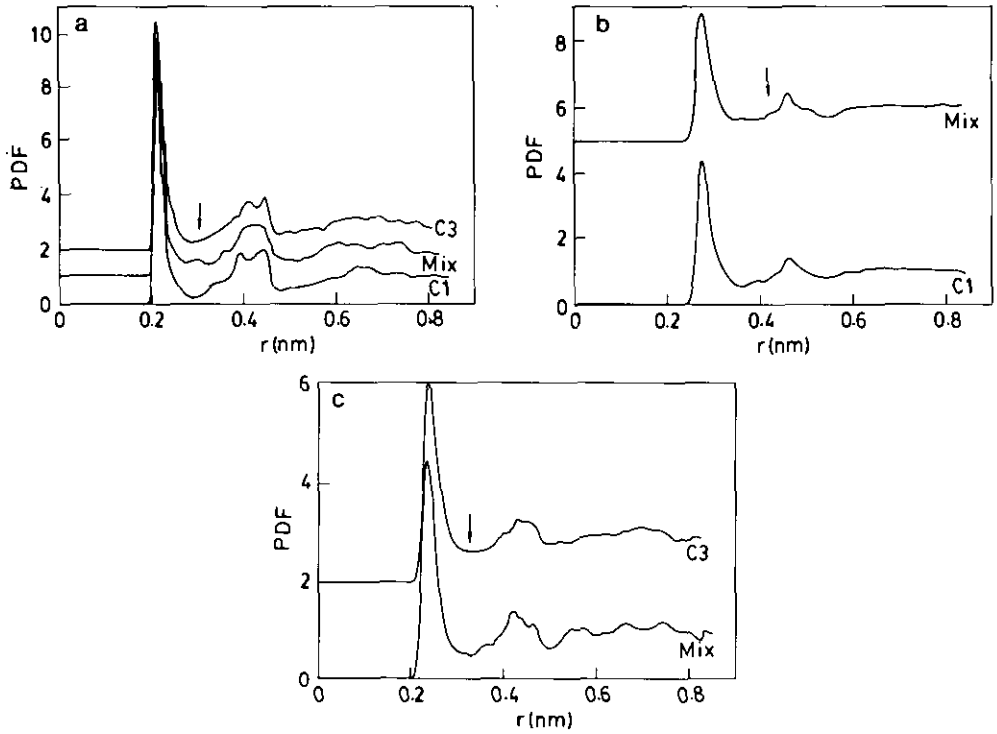

FIG. 1. Pair distribution functions of (a) Zn–O, (b) K–O, and (c) Na–O at 300 K for the various compositions. The arrows denote the position for coordination cut-off.

to as pseudospherical ions; they are considered as randomly close packed. Cations are randomly filled into the voids (whose numbers are far in excess) and local rearrangements are effected keeping in view the charges and sizes of the cations. Since the q/r ratio of Zn^{2+} ion is large, a rearrangement of sulfate ions occurs around

TABLE III

THE OXYGEN COORDINATION TO THE CATIONS AS OBTAINED FROM THE RESPECTIVE PAIR DISTRIBUTION FUNCTIONS (SEE FIG. 1)

Pair	Composition	First peak position (Å)	Coordination
Zn–O	C1	2.125	6.1 (2.875)
	C3	2.15	6.7 (2.9)
	MIX	2.15	6.3 (2.8)
K–O	C1	2.775	12.0 (4.25)
	MIX	2.8	12.0 (4.2)
Na–O	C3	2.375	8.0 (3.35)
	MIX	2.325	8.0 (3.55)

Note. The numbers in parentheses are the distances (the minimum in $g(r)$) in Å where the coordination cut-off is chosen.

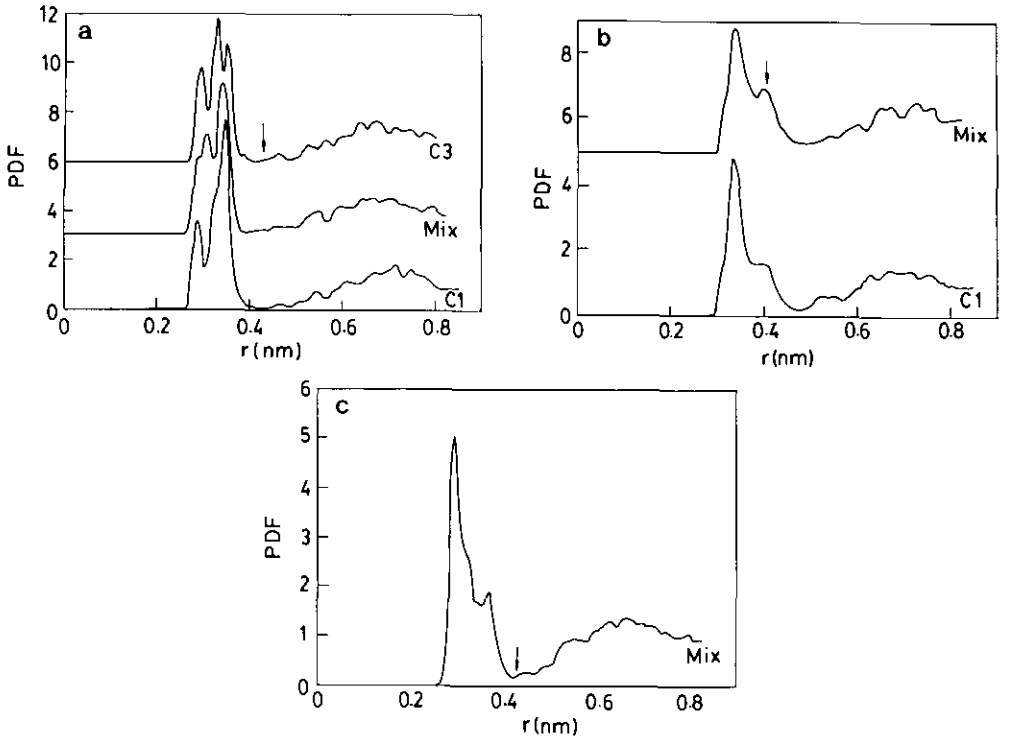

FIG. 2. Pair distribution functions of (a) Zn–S, (b) K–S and (c) Na–S at 300 K for the three compositions. Note the unsymmetrical first peak (see text for discussion).

TABLE IV

THE SULFUR COORDINATION TO THE CATIONS AS OBTAINED FROM THE RESPECTIVE PAIR DISTRIBUTION FUNCTIONS (SEE FIG. 2)

Pair	Composition	First peak position (Å)	Coordination
Zn–S	C1	2.875	
		3.475	5.3 (4.3)
	C3	2.975	
		3.325	5.5 (4.125)
		3.525	
	MIX	3.1	
		3.45	5.4 (3.9)
K–S	C1	3.35	4.0 (4.075)
	MIX	3.4	4.0 (4.075)
Na–S	C3	3.075	
		3.45	5.0 (4.4)
	MIX	2.975	
		3.7	4.3 (4.225)

Note. The numbers in parentheses are the distances (the minimum in $g(r)$) in Å where the coordination cut-off is chosen.

them and in the process, Zn^{2+} ions acquire an octahedral coordination with oxygen ions belonging to six different SO_4^{2-} ions. Octahedral coordination of zinc was known from probe ion spectroscopy (*4, 12, 13*) and was therefore built into the model. Rearrangement around potassium and sodium were thought to involve only a slight tilting of the SO_4 tetrahedra so as to enable Na^+ and K^+ ions to fit snugly into the voids, thus enabling them to acquire coordinations of 8 and 12 oxygen ions respectively from just 4 sulfate ions. Such coordination numbers are considered as ideal because the radius ratios, (r_{Na^+}/r_{O^-}) and (r_{K^+}/r_{O^-}) were 0.73 and 1.01, respectively. The rearrangement around Zn^{2+} ions changes gradually the nature of rcp of pseudospherical SO_4^{2-} ions as $ZnSO_4$ concentration in the glass increases. Toward the limit of a hypothetical $ZnSO_4$ glass, it would appear as if it is a modified random close packing of O^{2-} ions with sulfur ions occupying an appropriate number of tetrahedral voids making no addition to the volume (see (*2*) for details). The modification referred to above is with regard to octahedral coordination of Zn^{2+} ions. Small changes in volume occur when structural rearrangements occur and the resulting molar volumes of glasses are found to be in good agreement with the observed values.

In the present MD simulation the only built-in constraint from experiments is the glass density. Surprisingly, MD results bear out all important features of the structural model described above. It is seen from Table III that the average coordination number of zinc is close to 6 in all the compositions and the coordination numbers of sodium and potassium are also close to 8 and 12 respectively. In the computer quenched glasses where the quenching rates are of the order of 10^{12} K/sec, we expect substantially higher level of disorder involving large local distortions in spite of using only nondirectional coulombic forces. Even a well annealed glass would therefore possess local distortions significantly higher than what is implied in theoretical models.

The present level of agreement between the MD results and the expectations of the model are therefore considered very satisfactory in respect of the coordination numbers of cations. The numbers of SO_4^{2-} ions surrounding the Zn^{2+} cations is inferred from a Zn–S pair distribution function. The Zn–S PDF is shown in Fig. 2a. It exhibits a split character in all the three compositions with roughly similar intensities of the two peaks. The total number of neighbors computed from the area under the split peak for the three compositions are listed in Table IV. The numbers are closer to 6 than to 4 implying that the oxygen coordination of zinc is provided by six different SO_4^{2-} ions and not just four. The splitting of the PDF peak is a consequence of the local distortions brought about by the crowding of SO_4^{2-} ions around Zn^{2+} ion which effectively screens the positive charge of the latter.

However, the sulfur coordination numbers of K^+ and Na^+ (Table IV) are close to 4 (in pure Na_2SO_4–$ZnSO_4$ glass, it seems to be slightly higher). The number of sulfate ions coordinating to K^+ and Na^+ ions is therefore four each which is precisely a requirement of the structural model. Both in K–S and Na–S PDFs (Figs. 2a and 2b) reveal that the alkali–sulfur peaks are split and unsymmetrical, again indicating distortions in the coordination polyhedra. The S–S spatial correlations (not shown) are broad and diffuse and are important factors in preventing long range order. Thus we conclude that the structural features of a modified random close packing model proposed for the sulfate glasses (*1*) are well supported by the MD simulation of this work.

Radial Distribution Function (rdf) of the Sulfate Glasses

The total rdf's were obtained from the MD simulation by a convolution of all 10 pair distribution functions, K–K, K–Zn, K–O, etc. They are presented in Fig. 3 for the cases of C1 and C2 glasses. They are compared with the experimental rdf's ob-

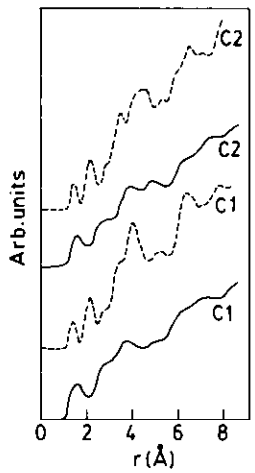

FIG. 3. Comparison of the radial distribution functions for glasses C1 and C2. The continuous lines are from (*3*) while the dotted ones are from the present MD simulation.

tained from X-ray diffraction (XRD) (*3*). The distribution functions from MD were weighted with known scattering factors for the various atoms and have been plotted as $4\pi r^2 \rho(r)$ for the simulated glasses. The first three peaks were assigned for S–O, Zn–O, and K–O in the XRD work. As can be seen from Fig. 3, the simulation results compare very satisfactorily with experimental rdf's. Hence we find that the very favorable comparison of the experimental XRD and MD results of the structure of sulfate glasses justify the potential parameters employed in the simulation.

Mixed Alkali Glass Compositions

We have examined the structures of mixed alkali glass compositions by considering appropriate interalkali pair distribution functions. We observe generally that the first peak in the like alkali ion (K–K and Na–Na) pdf (not shown) of mixed alkali glasses is slightly unsymmetrical and diffuse. Further, inspite of large simulation time and averaging employed in these simulations, the peaks are noisy. In the mixed alkali compositions the total number of like ions (K^+ around K^+ and Na^+ around Na^+) in the coordination sphere decrease. Thus for example, the number of sodium ions in the first sodium coordination shell of sodium ion is 6.03 in the binary C3 glass while it is 3.0 in the MIX glass. A similar decrease in coordination number has been observed in the K–K pdf between C1 and MIX. However, the decrease in coordination number is only about 25% rather than 50% (5.8 to 4.5). We consider the numbers as only approximate since the corresponding peaks in the pdf's were very noisy.

The dissimilar alkali correlation, namely K–Na, in the mixed alkali glass seems to be rather significant. We have shown in Fig. 4 the corresponding pair correlation function. Under the same conditions of data accumulation as employed in earlier class (K–K and Na–Na) the K–Na pdf shows a rather sharp peak at 3.88 Å with a coordination number of 2.6. It appears to us that in mixed alkali glasses, this interalkali ion correlation is of great significance. The symmetrical nature of the peak along with the absence of noise indicate that dissimilar alkali pairs become immobilized at some short and well correlated distances in mixed alkali glasses. It is possible that the requirement of optimal packing could cause this high degree of correlations.

Mean squared displacements (MSD) were evaluated for the systems as described ear-

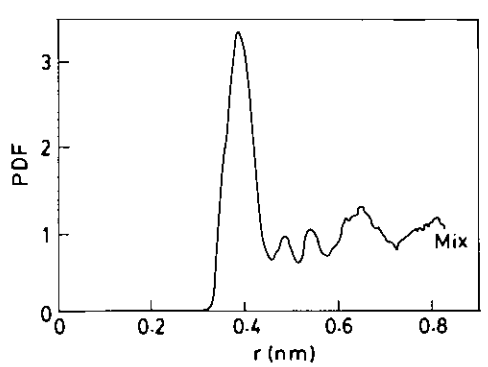

FIG. 4. Dissimilar alkali (K–Na) pair distribution function at 300 K in the mixed alkali glass. Note that the first peak is sharp indicating strong local ordering of the ions.

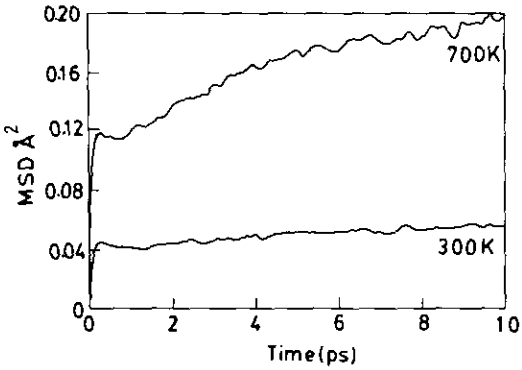

FIG. 5. Mean squared displacement data of sodium ions in the C3 composition. At 300 K, the sodium ions diffuse little and hence the system is in a glassy state.

lier. For the ion motions, drastic changes occur when the system is quenched from 700 to 300 K. Typically, the diffusion coefficient drops by two orders of magnitude. In Fig. 5 the MSD of Na^+ ions is shown at two temperatures (700 and 300 K) which clearly indicates that glass transition has already occurred above 300 K. Similar behavior was observed for all the ions in the glass.

A study of the dynamics demonstrates quite well the so called mixed alkali effect in these glass systems. The MSDs of all the cations (Zn^{2+}, K^+, Na^+) at 700 K have been shown in Fig. 6 for the relevant binary and mixed alkali compositions. Diffusion coefficients calculated for the ions are listed in Table V. The entries reading zero correspond to diffusion coefficients far less than 10^{-10} cm²/sec (three orders of magnitude less than the quantities finding entry in the table). It is readily seen that the diffusion coefficients of all the cations decrease in the mixed alkali composition and most notably of the alkali ions. Since diffusion coefficients are extremely low in the glassy state, the accuracy of the computations is very low at 300 K compared to the same at 700 K. Hence diffusion coefficients at 700 K are reported in Table V. The values well illustrate the mixed alkali effect; that is, the diffusion coefficient of the alkali ions drastically decrease when they are present together. Diffusion coefficients are clearly (Table V) much higher when they are present singly. Mixed alkali effect in conductivity had been earlier reported by us for the case of sulfate glasses (*14, 15*). We proposed at that time that packing geometries affect the doorways (required for passage of ions) unfavorably when two different types of alkali ions are present. Molecular dynamics simulation reported here fully supports the suggested mechanism. When we consider together the two observations, (i) sharp decreases in the magnitude of diffusion coefficients and (ii) presence of sharp peak in the dissimilar alkali pair distribution peak (Fig. 4) at 3.88 Å, we are led to conclude that, in ionic glasses, packing requirement is the principal factor in causing the mixed alkali effect.

Velocity Autocorrelation Functions

The velocity autocorrelation functions (VAFs) (based on the motion of the center of mass for the case of (SO_4^{2-}) ions) for the MIX glass are given in Fig. 7. We notice that the zinc ion motion is dominated by most persistent undulations about 0 in the VAF. It is understandably due to its confinement in its cage. VAF of K^+ ions is characterized by the longest undulation time scales but the VAF tends quickly toward 0. The undulations observed in the VAF of SO_4^{2-} ions seem to reflect the totality of its dynamical response to the cation motions. It is very interesting to note that in mixed alkali glasses the sodium ions exhibits a VAF essentially similar to that of zinc ions in spite of the large differences in the ionic potentials and hence the interaction strengths of the two ions. However, the differences in the masses seem to work in a manner that cancels the effect of the large differences in the ionic strengths. This feature is particularly clear in the infrared spectra where it has been observed that cage vibration frequencies of Na^+ and Zn^{2+} are rather close. The cation oscillations of VAF around 0 in mixed glasses over longer times also confirm that the alkali ions tend to confine to cages (immobilization). The Fourier

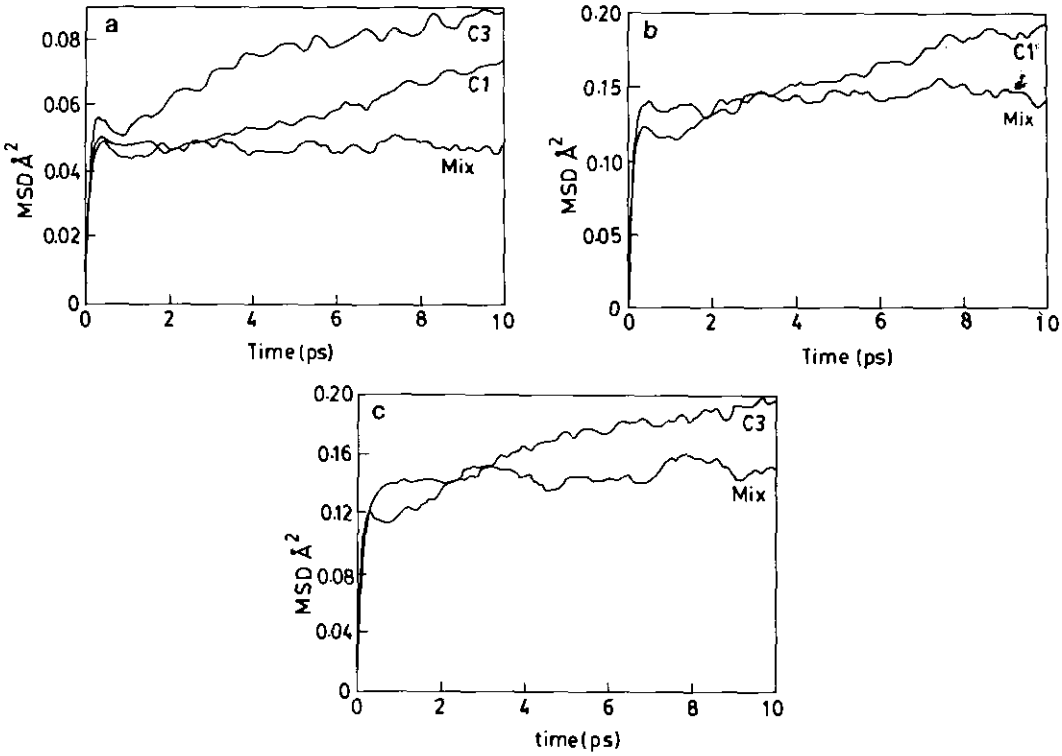

FIG. 6. Mean squared displacement data at 700 K of (a) zinc (b) potassium, and (c) sodium ions in the various compositions studied. Note the sharp fall in slope of the curves in the mixed alkali compositions (the mixed alkali effect).

tranform of the VAF of the Zn^{2+}, Na^{+}, and K^{+} ions give respectively broad peaks at 290, 253, and 156 cm^{-1}. The values of these cage vibrational frequencies may be compared with the 235-cm^{-1}, 227-cm^{-1}, and 202-cm^{-1} vibrational frequencies observed experimentally (*16*).

TABLE V

DIFFUSION COEFFICIENTS OF THE CATIONS AT 700 K IN THE VARIOUS GLASSES AS CALCULATED FROM THEIR MEAN SQUARED DISPLACEMENTS

Composition	Zn^{2+}	K^{+}	Na^{+}
C1	6.25	10.5	—
C3	6.78	—	15.08
MIX	0.0	0.0	3.2

Note. All data in units of 10^{-8} cm^2/sec.

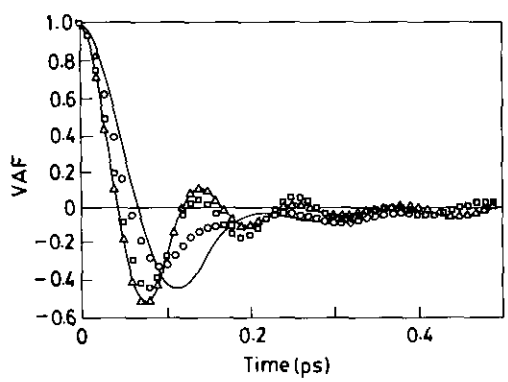

FIG. 7. Velocity autocorrelation function at 300 K of all the species present in the MIX glass. Though the data were evaluated up to 10 psec, only the short time region is shown here to highlight the negative correlations due to the "cage effect." (□) Zn; (—) K; (○) (SO_4); (△) Na. The continuous line through the triangles is to be used only as a guide to the eye.

Conclusions

Salient features of molecular dynamics investigation of the sulfate glasses have been presented and discussed in the background of the modified rcp model of sulfate glass structures proposed in earlier investigations. The simulation has provided significant support of the structural model. It has provided new insight to the origin of mixed alkali effect in sulfate glasses by revealing the presence of strong short distance spatial correlation of dissimilar alkali ions. The present simulation work has used charges on the various ions which were reported by Impey *et al.* (*8*). These are adjusted charges which match with the formal charges on the various cations and on the sulfate anion. We believe that the use of these charges on the various ions or any further adjusted charges will not materially affect our calculations.

Sir John Thomas visited our laboratory in Bangalore in 1980 when much of the experimental work and the modeling studies on sulfate glasses were being performed. He had shown keen interest in this work. It is therefore a pleasure for us to dedicate this paper to Sir John on the occasion of his sixtieth birthday.

Acknowledgment

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