SAND2000-1098 J

RECEIVED
JUN 06 2000
OSTI

Molecular Dynamic Simulations, ^{6}Li Solid State NMR and Ultraphosphate Glasses[†]

Todd M. Alam
Sandia National Laboratories
Albuquerque, NM 87185-1407

Our laboratory continues to use NMR to investigate the structure and dynamics in amorphous materials, including the local structure of ultraphosphate glasses. Changes in the alkali environment in these phosphate glasses as a function of modifier concentration has recently been probed using ^{6}Li and ^{23}Na solid state NMR.[1,2] Molecular dynamic (MD) simulations have also been performed in an attempt to gain additional insight into the variations of the local structure.[3] For example, Figure 1 shows a pictorial representation of the glass structure obtained from MD simulations.[3]

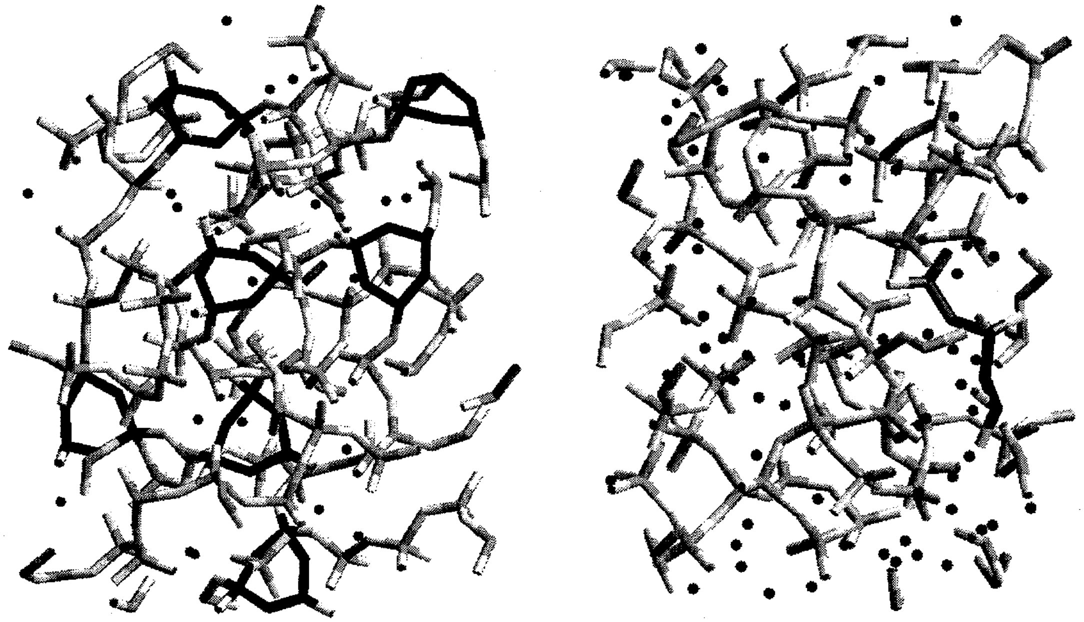

Figure 1: MD simulated structure for 20 and 50% Li_2O in $xLi_2O \bullet (100-x)P_2O_5$.

Interestingly, although there are distinct variations in the Li coordination number as well as the Li-O bond lengths in the MD simulations (with a minimum or maximum in these parameters near the 20% Li_2O concentration), a linear change in the ^{6}Li NMR chemical shift is observed between 5 and 50% Li_2O mole fraction. One would expect that such variations should be observable in the NMR chemical shift. In an attempt to understand this behavior we have performed empirical calculation of the ^{6}Li NMR chemical shift directly from the structures obtained in the MD simulations. It has been argued that the NMR chemical shift of alkali species can be related to a chemical shift parameter *A*,

---

[†] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

where A is defined as the summation of the shift contributions for all the oxygens located within the first (and possibly the second) coordination sphere around the cation.[1] For the present case of Li phosphate glasses, the chemical shift correlates directly to the bond valence of the coordinating oxygen. An empirical bond valence (s_{ij}) between oxygen i and the cation j can be calculated from the cation-oxygen bond length, r_{ij}, using

$$s_{ij} = \exp\left[\left(r_0 - r_{ij}\right)/B\right] \tag{1}$$

where r_0 is the empirically derived oxygen-cation bond length of unit valence, and B = 0.37 is a constant. The total valence of the ith oxygen (W_i) is simply the summation over all oxygen-cation bond valences s_{ij} for each of the j cations bonded to the oxygens, including both lithium and phosphorous cations:

$$W_i = \sum_j s_{ij} \tag{2}$$

The chemical shift parameter A is then be a summation of the oxygen shift contributions and assumes a $1/r_i^3$ dependence (where r_i is the Li-O bond distance):

$$A = \sum_i \frac{W_i}{r_i^3} \tag{3}$$

Recently we reported an empirical linear relation ship between the observed ^{6}Li chemical shift (δ_{CS})and the chemical shift parameter A for lithium phosphate system,[1]

$$\delta_{CS}(^6\mathrm{Li}) = +4.30A - 5.85 \tag{4}$$

Using Eqs. 1-4 the average ^{6}Li chemical shift was calculated from the MD structures as a function of Li_2O concentration, the results are shown in Figure 2. The observation of similar slope and similar chemical shifts is very promising. The offset can be controlled by variation of the cutoff distance used in the calculation of A. In this case, a 3.5 Å cutoff distance was utilized, the same as utilized in the development of Eqn. 4.[1] Even though there are minimum and maximum in the coordination number and the Li-O bond length, respectively; these effects are not observed in the resulting Li chemical shift. From Eqn. 3, if the average coordination number increases then the parameter A increases. From the MD simulations it appears that when this occurs, the Li-O bond distance also increases, thereby decreasing A. These two counteracting effects tend to cancel out any distinct minimum or maximum to produce a linear variation in chemical shift. Experimentally, this would suggest that subtle changes in the Li environment may be difficult to observe by Li NMR, since the chemical shift is a function of two different variables, and in some instances may produce changes that cancel out. A more detailed account of this work has been submitted and should appear soon.

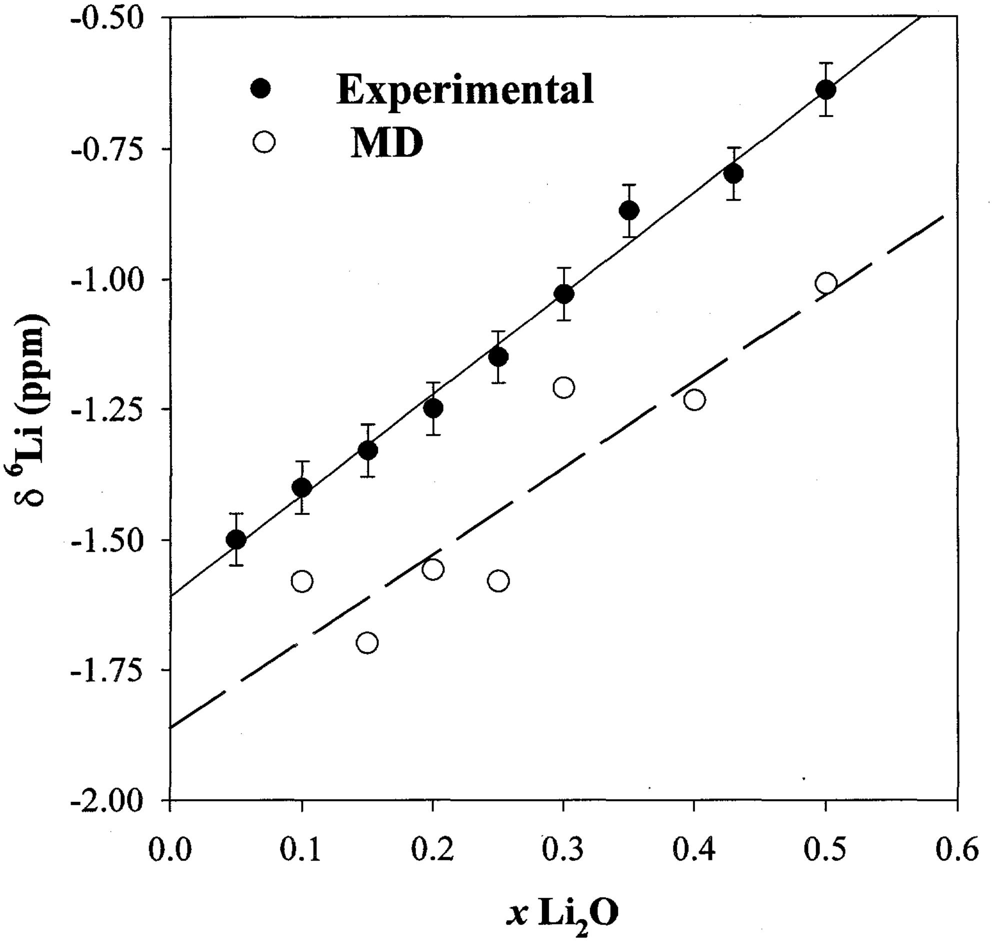

Figure 2: Variation of the ^{6}Li MAS NMR chemical shift, both experimental and predicted from the MD simulation, within a lithium ultraphosphate glass series as a function of Li_2O concentration.

[1] T. M. Alam, S. Conzone, R. K. Brow, T. J. Boyle, J. Non-Cryst. Solids 258 (1999) 140-154.

[2] T. M. Alam, J. McLaughlin, C. C. Click, S. Conzone, R. K. Brow, T. J. Boyle, J. W. Zwanziger J. Phys. Chem. (2000) 104, 1464-1472.

[3] J. J. Liang, R. T. Cygan, T. M. Alam, J. Non-Cryst. Solids (2000) 263&264, 167-179.