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Near-edge x-ray-absorption fine-structure spectroscopy investigation of poly(ethylene oxide)-KI complexes

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We have measured the near-edge x-ray-absorption fine-structure spectra of the *K* edge of potassium in the polymer-salt complex poly(ethylene oxide)-KI. Changes are observed as a function of temperature due to modifications of the K-ion coordination. Comparison with model systems suggests that the lower activation energy of this ionic conducting polymer complex at elevated temperature ($T > 70\,^{\circ}\mathrm{C}$) is partially due to reduced oxygen complexation of the K ions.

Ion conducting solids have been the object of intense study motivated by the possibility of electrochemistry without inconvenient liquid solvents. Historically, solid-state ion conductivity has been studied primarily in inorganic materials, such as β-alumina and silver salts.[1,2] However, since the discovery of ionic conductivity in poly(ethylene oxide) (PEO) complexed with alkali-metal salts,[3,4] research on this class of materials has grown rapidly. An important near-term application is the fabrication of high-energy-density rechargeable lithium batteries. However, the relationship between ionic conductivity and the microscopic structure of polymer-salt complexes is not well understood. Originally, it was suggested that ionic conduction in PEO was due to cation hopping within the helical PEO crystal structure,[4] reminiscent of the hopping responsible for ion conductivity in inorganic materials. However, later work showed that in the polymer complex, which consists of crystalline and amorphous phases, the ionic conductivity is associated with the amorphous phase,[5,6] not the crystalline phase. This implies that the conduction mechanism for this polymer complex is quite different from that for inorganic materials.

In the PEO-salt system the alkali-metal cation and the oxygen atoms in the ether group form complex in which the oxygen atoms form a "cage" around the cation, leading to dissociation of the anion-cation pair. The complexation is reversible, resulting in ionic conductivity.[7] Therefore, studying the complexation is crucial for understanding the ionic conductivity. However, the absence of long-range order in the amorphous phase responsible for conductivity precludes investigations of the microscopic structure using conventional x-ray diffraction. X-ray absorption spectroscopy, on the other hand, especially near-edge x-ray-absorption fine structure (NEXAFS) is sensitive to local structural properties such as interatomic spacings and coordination number, even in the absence of long-range order, and it is therefore well suited to a study of the amorphous conducting phase. In particular, by using the alkali atom as an absorber, the structure of the cation-polymer complex can be studied.

The ion transport properties of the polymer-salt complex are strongly dependent on the freedom of movement and rearrangement of the polymer chain.[7] This is described by the VTF (Vogel-Tamman-Fulcher) equation based on the free volume theory:

$$\sigma = A T^{1/2} \exp[-E_a/(T-T_0)] ,$$

where E_a is the pseudoactivation energy, T_0 is related to the experimentally measured glass transition temperature T_g by a constant, and A is proportional to the carrier concentration. The conductivity of PEO-KI complexes for three different concentrations of KI is plotted as a function of temperature in Fig. 1. Since the conductivity is plotted as $\ln\sigma$ versus $1/T$, the slope of the curve is proportional to the pseudoactivation energy E_α. The change of slope around 60–80 °C is an indication of a change of activation energy in this temperature range.

We report here the first systematic study of the temperature dependence of the NEXAFS above the *K* edge of potassium in the PEO-KI complex. The observed NEXAFS spectra exhibit important changes in intensity with temperature and KI salt concentration, which we interpret by comparison with reference systems in which K is coordinated with oxygen atoms ranging from 3 to 6. We

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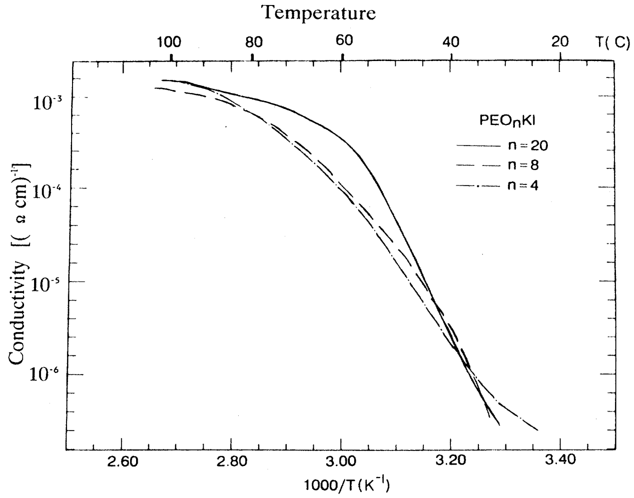

FIG. 1. ac conductivity of $(PEO)_n$-KI complexes, where n is the ratio of oxygen atoms to potassium ions.

tentatively conclude that the observed changes in the near-edge region are due to breaking of the symmetry of the local electric field in the vicinity of the K ion caused by a reduction in the oxygen coordination number with increasing temperature.

Poly(ethylene oxide) (PEO) with an average molecular weight of 600 000 and of 99.5% purity was obtained commercially (Aldrich Chemical). Reference compounds, including potassium iodide (KI), potassium tert-butoxide [$(CH_3)_3COK$], potassium acetate ($C_2H_3O_2K$), and dibenzo-18-crown-6 ($C_{12}H_{24}O_6$, 18-crown-6) of similar purity were obtained from the same source. Complexes of PEO-KI and 18-crown-6–KI were formed in acetonitrile solution and then cast as a film about 100 μm thick on Kapton tape. The other reference compounds $(CH_3)_3COK$, $C_2H_3O_2K$, and KI, in the form of fine powders, were brushed on Scotch tape.

Most measurements were performed at beam line X23B of the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY), using a Si(200) double-crystal monochromator. The harmonic intensity was monitored and minimized by detuning the monochromator when appropriate. Some measurements were also made at beam line C3 of the Cornell High Energy Synchrotron Source at Cornell University (Ithaca, NY). The absorption was computed as $\ln(I/I_0)$, where I_0 is the x-ray flux incident on the sample and I is the transmitted flux, both measured by ionization chambers using a mixture of helium and nitrogen gas. A smooth background has been removed from the data shown here. Spectra were obtained with the sample at 25, 50, 75, and 100 °C.

Figure 2 shows the x-ray absorption above the K edge of K in (a) KI and (b) a PEO-KI complex with a 20:1 oxygen:potassium ratio at 25 and 100 °C. The large "white line" feature evident above the edge is due to dipole-allowed transitions to final states of p symmetry,[8,9] and its prominence is indicative of the high density of such states in the PEO-KI complex. The KI spectra are the same at both temperatures as expected because the salt undergoes no phase transition in this temperature range. The spectra of the PEO-KI complex exhibit little temperature dependence, indicative of the lack of important structural or electronic changes with temperature in the vicinity of K at this low concentration.

In contrast to the lack of changes observed at low salt concentration, there are significant temperature effects at higher concentrations. Figure 3 shows the NEXAFS spectra of PEO-KI with oxygen:potassium ratio of 4:1 at four different temperatures. The single broad white line

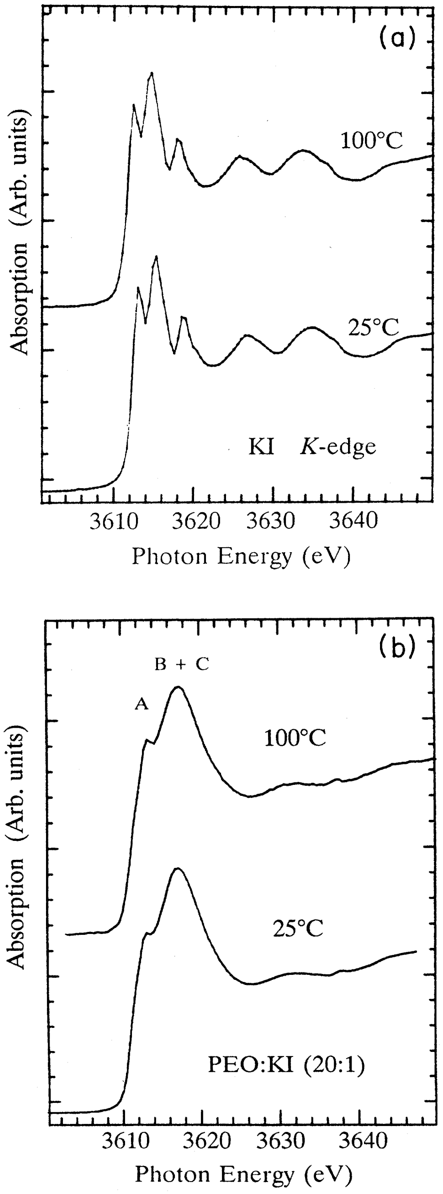

FIG. 2. (a) Near-edge x-ray-absorption spectrum of the K edge of potassium in KI at two temperatures as indicated. (b) Similar spectrum of potassium in $(PEO)_{20}$/KI at the same two temperatures.

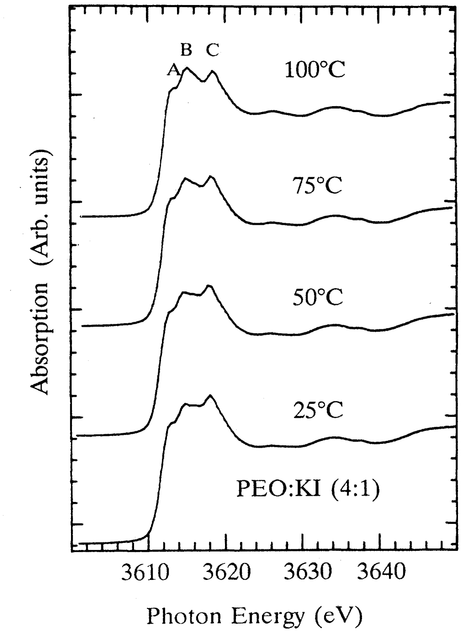

FIG. 3. Near-edge x-ray-absorption spectrum of the *K* edge of potassium in $(PEO)_4/KI$ at several temperatures as indicated.

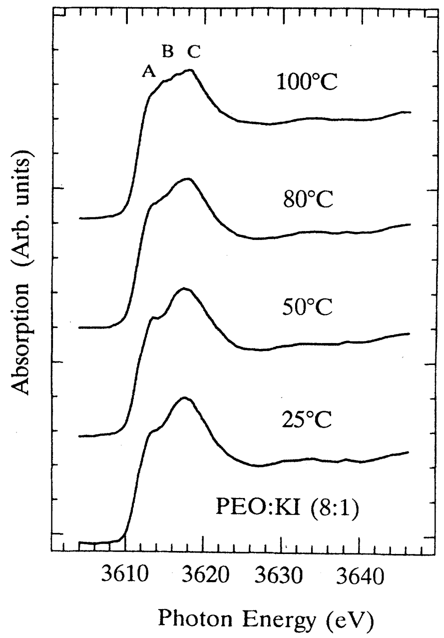

FIG. 4. Near-edge x-ray-absorption spectrum of the *K* edge of potassium in $(PEO)_8/KI$ at several temperatures as indicated.

in the 20:1 PEO-KI spectra has split into two peaks, which we label *B* and *C*, at about 4 and 7 eV above the absorption edge. The lower energy peak *B* increases with increasing temperature at the expense of the higher energy peak *C*, indeed becoming the dominant peak at 100 °C. The feature labeled *A* remains unchanged from the spectrum corresponding to the 20:1 complex.

For the intermediate salt concentration of 8:1 oxygen:potassium ratio, the NEXAFS spectra at four different temperatures are shown in Fig. 4. The temperature dependence is similar to that observed in the 4:1 complex; that is, peak *B* increases with increasing temperature. However, the magnitude of these changes is significantly less in this case.

The interpretation of these spectral changes is complicated by the fact that it is not appropriate to assign individual spectral features to particular transitions for potassium NEXAFS spectra, as is commonly done for low *Z* atoms such as carbon and oxygen.[10] In order to relate these changes to the microscopic structure of the PEO-KI complex, we examine the spectra of selected reference systems.[9] Figure 5 shows the spectra of three reference systems, namely $(CH_3)_3COK$, $KC_2H_3O_2$, and KI–18-crown-6 in which the potassium is coordinated with from 3 to 6 oxygen atoms. The potassium *tert*-butoxide $[(CH_3)_3COK]$ forms a terameric structural unit with potassium and oxygen atoms at alternate corners of slightly distorted cubes surrounded by the *tert*-butyl groups along the diagonals.[11] The K ion is coordinated with three oxygen atoms at the nearest corners of the cube with a 2.56 Å bond length. No detailed crystallographic study of the potassium acetate $(KC_2H_3O_2)$ is available. However, x-ray diffraction study[12] of the similar compound sodium acetate $(NaC_2H_3O_2)$ shows that the Na ion is surrounded by six oxygens at distances of 2.35 to 2.67 Å. Two of these six O belong to the same acetate ion while the other four belong to four different acetate ions. Assuming that the crystal structure is similar, in potassium acetate the

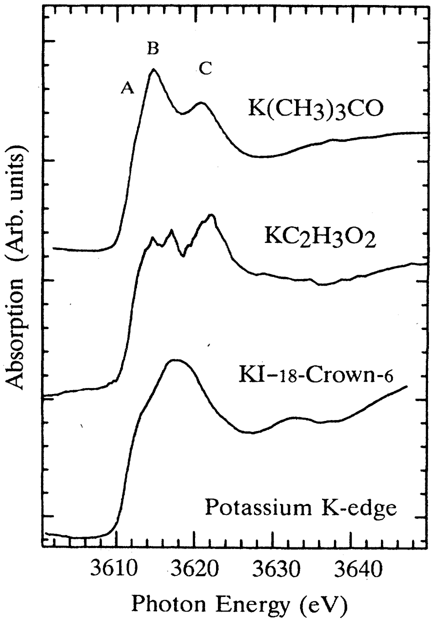

FIG. 5. Near-edge x-ray-absorption spectrum of the *K* edge of potassium in several reference compounds: $(CH_3)_3COK$, $C_2H_3O_2K$, and dibenzo-18-crown-6/KI at 25 °C.

K ions are coordinated with two nearest oxygens and four next-nearest oxygens. In the dibenzo-18-crown-6–KI complex, the K ion, located at the center of a nearly coplanar ring of six oxygens,[13] is coordinated with six oxygens. It is apparent from Fig. 5 that as the oxygen coordination number decreases from 6 to 3 in the sequence KI–18-crown-6, $KC_2H_3O_2$, $(CH_3)_3COK$, the intensity of the higher energy peak C decreases relative to that of the lower energy peak B. Similar changes in the near-edge white line features above the potassium K edge as a function of oxygen coordination number have been observed by Spiro *et al.*[9]

We now consider what may be concluded from the spectral changes with temperature observed in Fig. 3. Purely electronic factors, such as a change in the oxidation state of the absorber, will affect the shape of the absorption edge.[14] Since K has only one ionization state (K^+), this effect may be ruled out. Rather, the observed changes are probably due to variation in the local structural environment of the K^+, that is, changes in the number and kind of atoms in its vicinity. Such changes affect the NEXAFS both directly, by modifying the multiple scattering which gives rise to the near-edge structure, and indirectly, as changes in the local structure after the hybridization and the symmetry of the molecular orbitals. In view of the decrease observed in the higher energy peak in Fig. 5 with decreasing oxygen coordination number, we conclude that the primary effect of increasing the temperature of the PEO-KI system at high salt concentrations is to reduce the oxygen coordination number around the K cation. As this reduction occurs in the same temperature region over which the activation energy of the conductivity decreases, it is natural to associate this structureal change with the reduction in activation energy.

The changes in the oxygen coordination number are associated with the breaking of symmetry around the K ions. As pointed out above, there is no simple correspondence between individual features in the absorption spectrum and the local environment of the absorbing atom. Rather, the local environment affects the shape of the absorption spectrum indirectly. The photoabsorption matrix element is determined, in view of the dipole selection rule, by the spatial overlap of the initial $l=0$ (K) core state with the $l=1$ angular momentum components of the unoccupied K and ligand (O) orbitals. Changes in the local environment affect the intermixing (hybridization) of these orbitals and thus the overlap. Moreover, changes in the local environment affect the crystal field experienced by these orbitals. When the absorbing atom is in a highly symmetric site, these orbitals may be energy degenerate, but as the symmetry decreases, the crystal field experienced by each of the degenerate states will be different and the degeneracy will be lifted. This gives rise to an energy splitting of the absorption edge. This effect was observed, for example, by Petiau and Calas, who found a splitting of the K edge of Fe in a series of compounds,[15] which increases as the Fe site symmetry decreases, and by Balzarotti, who observed a splitting of the Ti K edge due to breaking of the degeneracy of the t_{2g} and e_g levels in several Ti-based compounds.[16]

The effect of symmetry can be seen clearly in the three reference spectra of Fig. 5. In the 18-crown-6–KI system, the K ion is located at the center of a sixfold ring of oxygen atoms, a relatively symmetric arrangement in which there is little energy difference between the various orbitals. In this system, the near-edge region consists of a single broad peak. In crystalline $KC_2H_3O_2$, each K ion has two nearest-neighbor oxygens and four next-nearest-neighbor oxygens. Although the coordination number is still 6, the K site symmetry is reduced relative to the 18-crown-6–KI system, since as pointed out above all but two of the O atoms are more distance from the K ion. This broken symmetry splits the "white line" into two peaks B and C. In crystalline $K(CH_3)_3CO$, each K ion coordinates with three O ions which are all on one side of the K ion. In this highly asymmetric situation the intensity of peak C is decreased relative to peak B.

The near-edge spectrum of K complexed with PEO at a low concentration of 20:1 [Fig. 2(b)] most nearly resembles the 18-crown-6–KI spectrum of Fig. 5, indicating that these K cations are similarly coordinated with oxygens in an arrangement which statistically has high symmetry. This conclusion is in agreement with the standard model of polymer-salt complexes, where intermolecular and intramolecular complexation by highly flexible polymer chains allows a variable degree of complexation.[6] At low salt concentrations, it is possible for the PEO polymer chains to provide enough oxygen atoms to preserve the high symmetry of the K site even at elevated temperatures. Consequently, no splitting of the near-edge feature is observed and there is little change with temperature. At higher salt concentrations, on the other hand, the number of oxygen atoms for each K ion is limited. It is no longer possible, particularly at elevated temperatures, for the polymer chains to provide enough oxygen atoms to preserve the symmetry of the K site. The resulting asymmetry splits the degeneracy of the K and O orbitals and correspondingly produces a split near-edge peak, as observed in the spectrum of the 4:1 KI:PEO complex of Fig. 3 at room temperature. As the temperature is increases, the increase in free volume associated with the increases local mobility of the polymer chains further reduces the number of oxygens adjacent to the K ion and hence the symmetry of the K site. The effect, seen in Fig. 3, is to increase the intensity of the lower energy peak B. Just as in the reference spectra of Fig. 5, the intensity of the lower energy peak B increases as the site symmetry decreases.

The shoulder labeled A, on the other hand, does not change with the changing oxygen environment of the potassium ion, and is therefore probably not associated with a degenerate state. A similar, but less dramatic, effect is observed in the intermediate concentration 8:1 complex of Fig. 4, in which case the polymer chains are more able to provide the K ions with oxygens, resulting in increased symmetry of the complexation. We conclude therefore that the oxygen coordination number of the K ions decreases at high temperatures. This decreased coordination could increase the mobility of the K ions and be responsible for the lower activation energy of conductivity of the PEO:KI complex at elevated temperature.[7] However, no dissolution and recrystallization of the KI at elevated temperatures were observed for the highly concentrated 4:1 system. The near-edge features, even at 100 °C, do not resemble those of the salt. Moreover, our x-ray diffraction studies[7] revealed no evidence of crystalline KI.

In conclusion, we have found that the primary effect of increasing the temperature of the PEO-KI complex, particularly at high salt concentrations, is to reduce the oxygen coordination number of the K ion. This reduced K-O complexation and chain interlinking may be responsible for the lower activation energy of ionic conductivity at higher temperature. These results demonstrate the power of the NEXAFS technique in the investigation of amorphous systems.

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