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6 An Approach to Understanding the Mixed Alkali Effect

by

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20. Continued

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An Approach to Understanding the Mixed Alkali Effect

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Abstract

An approach to understanding the mixed alkali effect in binary ionic oxide glasses is proposed. It is based on an expression for the composition dependence of activated processes which is inherently cooperative, and employs the regular solution model for the specification of this dependence. A detailed molecular-level model, using spectroscopic data, is introduced to obtain an estimate of the magnitude of the parameters of the approach. It is shown that the composition dependences of the non-linearly varying properties of mixed alkali systems, including both the measured properties and the exponential and pre-exponential factors obtained from their temperature dependence, can be understood using this approach.

Introduction

Ionic oxide glasses of the general formula xM_2^AO (1-x) M_2^BO ApOq are commonly referred to as mixed alkali glasses when M_2^AO and M_2^BO are different network modifying alkali metal oxides and ApOq is a network former such as SiO_2, P_2O_5, B_2O_3 or GeO_2 the mixed alkali glasses are of special interest[1] because many of their physical properties vary extremely nonlinearly as x is varied. This has been shown clearly in a number of experimental investigations and discussed in several excellent review articles.[2-19]

Series of mixed alkali glasses are made by changing the relative concentrations of the alkali metal oxides while holding the overall stoichiometry constant (varying x in the general formula). The nonlinearities found[1] are most pronounced for properties related to ionic mobility such as electrical conductivity, ionic diffusion, and dielectric relaxation and loss. On the other hand, bulk thermodynamic properties, such as molar volume and density, refractive indices, thermal expansion coefficient, and elastic moduli vary either linearly with x or show only small deviations. Properties related to structural relaxation such as viscosity and glass transition temperature usually exhibit negative deviations. The nonlinear behavior of certain physical properties with respect to x in a series of mixed alkali glasses is generally known as the mixed alkali effect (or polycation effect).

Some of the previous theories of the mixed alkali effect can be characterized by noting some special postulate about the structural character of the glass network and have been proposed primarily to explain ionic conductance behavior. Each emphasizes alkali ion distributions or sizes, and each has some inadequacy such as the need for a large number of adjustable parameters, the inability to account for other properties of mixed alkali glasses, or simply the inability to explain the observed phenomena.

Others emphasize differences in the bonding and coordination of the alkali ions in different alkali mixed alkali glasses. Although these have some similarities to the structural theories, they commonly assume that some type of interaction between dissimilar alkali ions is responsible for the reduced cation mobility in mixed alkali glasses. Foremost among them is the theory of Hendricksen and Bray,[19] which emphasizes the importance of the interaction energy arising from the coupling of the oscillations of neighboring dissimilar ions in reducing the cation mobility. One other important aspect of this problem which other approaches have either neglected or provided unsatisfactory explanations for is the composition dependence of the preexponential (Arrhenius) term derived from experimental conductivity data.

Although there are structural consequences of changing the relative concentrations of the network modifying cations, and certain of the interactions discussed in previous approaches are undoubtedly present, previously reported approaches have a difficulty we wish to address with a new approach. The difficulty is that the cations, however their mobility is affected by the geometry or other cations, are treated with general equations which subtly and often implicitly assume that the statistical methods appropriate for independent cation motion events apply to the system. This is internally contradictory in those cases, especially those that postulate an interaction energy, in which the conductivity in mixed alkali glasses is assumed to be due to a cooperative process characterized by a concerted hopping mechanism involving both cations.

In this paper we present an approach to understanding the mixed alkali effect which overcomes these difficulties by recognizing that the relevant processes are inherently cooperative. Thus, it treats a general transport property such as conductivity, as a cooperative process characterized by a free energy of activation. In addition to presenting this general approach, we discuss a specific model, applying this approach, which provides for the evaluation of the composition dependent energy of activation for the conductivity process. This approach also provides an explanation for the composition dependence of the preexponential (Arrhenius) term. This specific model employs the spectroscopic (cation motion vibrational frequencies) observations of **our earlier study**[1] to evaluate the energies relevent to the proposed ionic transport model.

Theory

The general approach to the problem of describing the composition dependence of a transport property is based on the proposition that the relaxation time for the process characteristic of the property is determined by the probability of a cooperative rearrangement associated with the process. The approach is based, in part, on the Adam and Gibbs[20] approach describing the temperature dependent relaxation times associated with cooperative rearrangements in glass forming polymers. To evaluate the transition probabilities, a cooperatively rearranging region is defined as a subsystem of the sample which, upon a sufficient fluctuation in energy (or enthalpy) can rearrange into another configuration independently of its environment. A further assumption is that each subsystem interacts only weakly with the macroscopic system. Since the subsystems are in mechanical and thermal contact with each other, they can be considered as an isobaric, isothermal ensemble of N independent, equivalent, and distinguishable subsystems. The distribution of these subsystems is assumed to depart negligibly from an equilibrium distribution.

Now if these subsystems are sorted into two classes, those, n in number, which reside in states undergoing cooperative rearrangements, and the N-n that are in states not undergoing a transition, the fraction that is in states permitting rearrangement is given by

$$\frac{n}{N} = \frac{f'}{f} = \exp\left(-(G'-G)/RT\right) \qquad (1)$$

where f', G' and f, G are the partition functions and Gibbs free energies for rearrangeable subsystems and for the ensemble, respectively. The cooperative transition probability, W(T), is proportional to n/N, or

$$W(T) = A\exp(-\Delta G/RT) \qquad (2)$$

This expression represents the transition probability for a cooperative region, where A can be assumed negligibly temperature dependent in comparison with the exponential function, and $\Delta G = G' - G$. In the application of this approach to polymer systems, the subsystems were made up of polymer segments containing Z monomer units and the ΔG of equation (2) referred to the free energy change associated with a cooperative rearrangement of the Z monomer units in a polymer segment constituting a subsystem. In extending this treatment to other systems, the subsystems and free energy changes must be redefined to be consistent with the process of interest. For example, if the process is ionic transport in glasses, which will be discussed in detail in a later section, the subsystems would consist of some Z number of ions and their sites and the ΔG for the process would represent the free energy change associated with the cooperative rearrangement of these ions within a subsystem.

Now if this approach can be extended to the problem of the composition dependence of the transition probabilities in binary mixtures, a general approach to the problem of the mixed alkali effect will be firmly established. This extension can be carried out by assuming the binary mixture to be described by an appropriate mixture model and by replacing the free energies (G' and G) of equation (1) by their composition dependent counterparts derived from the mixture model, so that equation (2) is replaced by

$$W(T,x) = A\exp(-\Delta G(x)/RT) \qquad (3)$$

where x represents the compositional variable (for convenience it will be taken as the mole fraction of one of the components). Note that in this expression, all the composition dependence of the transition probability is embodied in $\Delta G(x)$. The behavior of a transport property, t, with respect to x can now be described as

$$t(x) = t_o \exp\ (-\Delta G(x)/Rt) \qquad (4)$$

where t_o is a constant independent of temperature and composition and the problem of expressing the composition dependence of a cooperative transport property in glasses is reduced to one of appropriately expressing the composition dependence of the change in free energy associated with the process characteristic of the property. It should be stressed here that the idea of cooperative as opposed to independent processes is fundamental to this approach.

The Composition Dependence of G

Applying this approach to finding the composition dependence of properties of mixed alkali glasses requires expressing the composition dependence of the molar Gibbs free energy of activation, $\Delta G(x)$.

In considering ways to do this it is helpful to note that the problem is similar to that for ionic conductivity and ionic self diffusion in binary mixed ionic crystals. These properties of mixed ionic crystals have been treated in a number of ways.[21] The simplest, based on Nernst type expressions that are valid only as limiting laws for infinite dilution of mobile ions, are qualitatively useful, but they lead to significant inaccuracies when applied to real systems. Thus, in these non-ideal mixed crystals, there are often differences between self-diffusion coefficients derived from electrical conductivity and those derived from interdiffusion experiments. Naturally, the usual explanation for the discrepancies is that mixed crystals deviate from ideal behavior. Accordingly, the diffusion equations have been rederived and the activity and activity coefficient introduced to take account of this nonideality.

Although this is appropriate in principle, measurements of activities for mixed crystals of ionic compounds are not usually available and a model is required to estimate them and obtain their functional dependence on x The model which has been employed successfully for this purpose is that of a regular solution.

On the basis of the application of the regular solution model to ionic conductivity and diffusion in non-ideal binary ionic crystal mixtures[21] and the success of approaches that use the model in treating the physical properties of liquid-liquid and solid-solid mixtures, the following assumption will be made. The mixed alkali glass system will be treated as a binary mixture, whose components are $M_2^AO \cdot ApOq$ and $M_2^BO \cdot ApOq$, and the regular solution model will be assumed in order to derive the composition dependence of $\Delta G(X)$. Recall that the ΔG is an activation free energy, defined in equations (1) and (2) and that the regular solution model applies separately to G' and G of equation (1).

The molar activation free energy, $\Delta G(x)$ is given by

$$\Delta G(x) = \Delta' G_{act}(x) - \Delta' G_{eq}(x) \tag{5}$$

where $\Delta' G_{act}(x)$ indicates the value of the free energy in the activated state (the n cooperatively rearrangeable subsystems) relative to a reference state and $\Delta' G_{eq}(x)$ is that for the N-n subsystems in states not undergoing a transition. For each there is a mixing term ΔG_M so that including the appropriately weighted pure component terms, they are given by:

$$\Delta' G_{act}(x) = x_A \Delta' G^\circ_{A,act} + x_B \Delta' G^\circ_{B,act} + \Delta' G_{M,act} \tag{6}$$

and

$$\Delta' G_{eq}(x) = x_A \Delta' G^\circ_{A,eq} + x_B \Delta' G^\circ_{B,eq} + \Delta' G_{M,eq} \tag{7}$$

Now, statistical treatments of regular solution models give rise to mixing terms (one for each of the two states -- activated and equilibrium) of the form

$$\Delta G'_M = RT\,(x_A \ln x_A + x_B \ln x_B) + x_A x_B\, J' \qquad (8)$$

where x_A and x_B are the mole fractions of components A and B, and J' is a characteristic energy parameter which is a measure of the deviation of the system from ideal mixture behavior.

The physical significance of J' in molecular models is clearly delineated as

$$J' = 2\Delta' E^\circ_{AB} - \Delta' E^\circ_A - \Delta' E^\circ_B \qquad (9)$$

where $\Delta' E^\circ_{AB}$ represents the contribution of A-B interactions, and $\Delta' E^\circ_A$ and $\Delta' E^\circ_B$ are the A-A and B-B interaction energies, respectively. These terms in the regular solution approximation arise from expressing the total interaction energy of the mixture in terms of the nearest neighbor pair interactions.

Placing equations (6) and (7) into (5) yields the expression for $\Delta G(x)$

$$\Delta G(x) = x_A \Delta G^\circ_A + x_B \Delta G^\circ_B + \Delta G_M \qquad (10)$$

where $\Delta G^\circ_A = \Delta' G^\circ_{A,act} - \Delta' G^\circ_{A,eq}$, $\Delta G^\circ_B = \Delta' G^\circ_{B,act} - \Delta' G^\circ_{B,eq}$, and $\Delta G_M = x_A x_B (J'_{act} - J'_{eq}) = x_A x_B J$. Note that the ideal mixing term $RT(x_A \ln x_A + x_B \ln x_B)$ drops out since it is the same for both the activated and equilibrium states. Now, by making use of standard relationships and assuming that $\left(\frac{\partial J}{\partial \ln V}\right)_T = 0$, equation (10) can be reexpressed in terms of separate energetic and entropic contributions:

$$\Delta G(x) = \left\{ x_A \Delta E^\circ_A + x_B \Delta E^\circ_B + x_A x_B \left[J - T \left(\frac{\partial J}{\partial T}\right)_{P,x} \right] \right\} - T \left\{ x_A \Delta S^\circ_A + x_B \Delta S^\circ_B - x_A x_B \left(\frac{\partial J}{\partial T}\right)_{P,x} \right\} \qquad (11)$$

where J is the effective interaction energy parameter. Expressing equation

(11) as

$$\Delta G(x) = E(x) - TS(x) \tag{12}$$

where E(x) and S(x) refer to the terms in the first and second set of curly brackets in equation (11) allows equation (4) to be expressed as

$$t(x) = t_o \exp\left([-E(x) + TS(x)]/RT \right) \tag{13}$$

or

$$\ln t(x) = [\ln t_o + \frac{S(x)}{R}] \; \frac{-E(x)}{RT} \tag{14}$$

Equation (14) has been rewritten in this way for the purpose of comparison with conventional expressions of this form in a later section.

The problem of expressing the composition dependence of a particular transport process now becomes one of finding the J, or interaction energy, characteristic of the particular transport process.

From equation (9) J of equation (11) can be expressed as

$$J = 2\Delta E^{\circ}_{AB} - \Delta E^{\circ}_{A} - \Delta E^{\circ}_{B} \tag{15}$$

The physical meaning of J for the transport process under consideration can be clarified by an examination of the method by which it is determined for a particular process.

For the molecular model under consideration, the energy barriers to transport of the ions cooperatively moving with three possible nearest neighbor interactions, A-A, B-B, and A-B, must be examined. The activation energy for each such pair is associated with the corresponding ΔE term in equation (15). For a particular pair of sites (A-A, B-B, or A-B), transport can proceed in either of two ways. In the case where the sites involved are the pair A-B, the two ways in which transport can occur are an A ion moving to a B site or a B ion moving to an A site and the corresponding ΔE term is an average of these two, or $\Delta E_{A-B} = \frac{1}{2} (\Delta E_{AB} + \Delta E_{BA})$.

When the two sites involved are A-A or B-B, however, the two ways in which transport can occur for each pair are equivalent and ΔE_A° and ΔE_B° are simply the activation energies for transport of the A and B ions to A and B sites respectively. From (15) it can be seen that J is related to the difference in activation energy associated with transport to dissimilar rather than similar sites.

Thus far, a general model applicable to the composition dependence of any transport property has been developed which allows for the determination of the composition dependence of a transport property once the characteristic interaction energy, J, for the process has been determined.

Vibrational Spectra of Ionic Oxide Glasses

Earlier,[1] several important observations of the vibrational spectra of single and mixed alkali glasses were presented. These observations will be summarized here.

The far infrared spectrum of each of a series of ionic oxide glasses $M_2^AO \cdot ApOq$ where M=Na, K, Rb, Cs contains a broad absorption band which has been assigned to the vibration of the cation in its site in the glass. It has also been shown[22] that the cation vibrational frequency, ν_o, is related to the activation energy for ionic conductivity by the expression

$$E_a = \frac{1}{2} M l_o^2 \nu_o^2 \qquad (16)$$

where M is the cation mass and l_o is the site-site distance (the distance the cation must hop to get to a nearest neighbor site). This relationship is used to evaluate the energies involved in ionic transport processes and will be discussed further in the next section.

The far infrared spectra of the glasses discussed earlier[1] show that the frequencies of the cation- motion bands in the far infrared spectra do not shift with x, indicating that the vibrationally significant local geometry and forces associated with a particular cation are unaffected by the introduction of a second cation into the glass structure. Each Raman active band due to vibrations of the metaphosphate network occurs at a different frequency for each pure glass (x=0 or 1), but for mixed alkali glasses only one band occurs for each type of mode and it varies linearly with x. This indicates that the cations in these mixed alkali glasses are homogeneously distributed, there is no cation clustering, and the phosphate chains are associated with an averaged cation environment whose effect on the chain modes varies with x. These general observations may be expected to apply to any ionic oxide glass system.

These spectroscopic observations are important to this approach for the following reasons: (1) In order for the regular solution theory employed in this approach to apply to transport processes involving ionic transport, the cations must be randomly distributed and the activation energies, ΔE°_A and ΔE°_B, must be composition independent. The spectroscopic observations are consistent with these requirements, and (2) a quantitative comparison of theory with experimental ionic transport data requires a method for evaluating the energy terms of equation (11) independently. The far infrared data provide a means of evaluating these energies.

Ionic Transport Phenomena

The conductivity of glasses is usually represented by the empirical equation

$$\ln\sigma = \ln\sigma_o - \frac{E_a}{RT} \qquad (17)$$

If $\ln\sigma$ is plotted as a function of 1/T for a particular glass, the preexponential term, $\ln\sigma_o$, and activation energy, E_a, can be determined from the intercept and slope of the resulting straight line. The conductivity behavior of mixed alkali glasses can be conveniently discussed in terms of equation (17) if the composition dependence is explicitly stated as

$$\ln\sigma(x) = \ln\sigma_o(x) - \frac{E_a(x)}{RT} \qquad (18)$$

In a typical mixed alkali glass system, $E_a(x)$ and $\ln\sigma_o(x)$ plotted vs. composition, x, exhibit maxima, and the maximum in $E_a(x)$ is larger than the maximum in $\ln\sigma_o(x)$ so that a minimum in $\ln\sigma(x)$ is always observed.

In comparing to results of our approach with experimental conductivity data, we find that the available ionic conductivity data must be divided into two categories:

(A) The ionic conductivity is known experimentally at only one temperature. In this case, $\ln\sigma_o(x)$ and $E_a(x)$ of Equation (18) are not known experimentally. Our approach allows for the calculation of $E_a(x)$ based on the measurements of the cation vibrational frequencies and calculation of ΔE_A, ΔE_B and J. In this case, we must assume that $\left(\frac{\partial J}{\partial T}\right)_{P,x}$ of (11) is zero and $\ln\sigma_o(x)$ is linear, since we have no method of determining $\left(\frac{\partial J}{\partial T}\right)_{P,x}$.

(B) The ionic conductivity is known experimentally at two or more temperatures for each glass in the mixed alkali series. In this case, $\ln\sigma_o(x)$ and $E_a(x)$ can be determined by application of Equation (18) to the experimental data. Our approach allows us to calculate $E_a(x)$, as noted above. Once $E_a(x)$ has been determined, $\left(\frac{\partial J}{\partial T}\right)_{P,x}$ can be assumed to be negligible (and $\ln\sigma_o(x)$ linear), or $\ln\sigma_o(x)$ can be estimated by using $\left(\frac{\partial J}{\partial T}\right)_{P,x}$ as a fitting parameter.

The details of this procedure will be discussed below.

A Molecular Model for Estimating J

The magnitude of the mixed alkali effect with respect to conductivity is determined by the interaction energy, J. So the problem of expressing the composition dependence of a particular transport process is primarily one of finding the characteristic interaction energy parameter, J, associated with the particular process. In order to determine the interaction energy, one must assume a model for the process and then evaluate the appropriate energy barriers to transport in a manner consistent with the proposed model. The magnitude of J depends on the ionic radii and masses of the alkali ions and increases as their differences increase. Several attempts have been made to correlate these effects with either the ionic radii or masses of the cations, but in this approach we suggest that both ionic radii and masses are important factors.

The present model, applicable to ionic oxide glasses of the general form $x_A M_2^A O$ $x_B M_2^B O$ ApOq where x_A, for purposes of consistency in the remainder of this section, designates the larger cation, considers the generally accepted ionic hopping model to apply to such transport processes as ionic conduction and diffusion. The characteristic interaction energy, J, can then be expressed in terms of the activation energies for cation site-site hopping. These activation energies for site-site hopping correspond to the activation energy terms discussed in the general approach. The values of the activation energies are arrived at from consideration of isolated nearest neighbor *pair* interactions as in the general model.

The energy barrier to transport of a cation from one site to a nearest neighbor vacancy which is large enough to accommodate the cation is given by an equation of the form of equation (16). (The site-site distances can be estimated from data for analogous crystalline materials and the cation vibrational frequencies can be determined from the far infrared spectra of the glasses.) This expression results from formulating the ionic hopping process in terms of a double potential well in which the cation acts as a simple harmonic oscillator in hopping from one well to the other. The validity of this expression has been tested with success for several glass systems.

For the three hopping processes involving the transport of a cation from its site to a vacancy of equal or larger size (A-A, B-B, B-A, where A is the larger cation) the activation energy is given by an expression of the form of equation (16). For the process involving transport of a large cation to a small site, however, an additional amount of work, w, must be expended to expand the small site so that it can accommodate the large cation. This additional amount of energy must be added to the activation energy for hopping so that the total activation energy for a large cation hopping to a small vacancy is given by an expression of the form of equation (16) plus an additional amount of work, w. This additional amount of work can be estimated by saying that it is equivalent to the work done in expanding the small site (a vacancy created by the departure of a small cation). This is equivalent to the energy required to move each of the six oxygen atoms a distance equal to $r_A - r_B$ against a force associated with k_{M-0}, the metal-oxygen force constant, where r_a and r_B represent the M-0 bond distances for the large and small cations, respectively.

$$w = 6\ [\frac{-1}{2} \int_0^{r_A - r_B} k_{m-o}\ rdr] \qquad (19)$$

Assuming that the cation site is octahedral (it is not, but this assumption is a reasonable approximation for determining the reduced mass of the oscillator) the additional work term, w, can be expressed in terms of the cation mass and vibrational frequency as

$$w = 6\ [\frac{-1}{2} \int_0^{r_A - r_B} 4.4\pi^2 \nu^2 \mu rdr] \qquad (20)$$

$$w = 13.2\pi^2 \nu^2 \mu\ (r_A - r_B)^2 \qquad (21)$$

where μ is the reduced mass of the large cation in an octahedral site of oxygen atoms ($\mu = MM_o/(2M_o + M)$). The expressions for the evaluation of the activation energies and interaction energies for ionic conduction and diffusion have now been expressed in terms of molecular properties of the glasses comprising the two components of the mixture. These molecular properties, cation masses, cation vibrational frequencies, and site-site distances can be independently determined.

The most striking feature of the mixed alkali effect with respect to conductivity is the apparently simple dependence on ionic radii (or masses). The effect increases dramatically as the difference in sizes (or masses) of the two alkali ions increases. This is shown quite clearly by the results of Hakim and Uhlmann[3] who studied the systems $x\ Cs_2O\cdot(1-x)R'_2O\cdot6.7SiO_2$ where R = Rb, K, Na, Li. The lowest maximum in $E_a(x)$ was observed for R = Rb and it increased regularly in the sequence R = Rb to R = Li. It has also been observed that the maximum in $E_a(x)$ and minimum in $\ln\sigma(x)$, which usually are observed at approximately the same composition, always occur at a composition rich in the larger alkali ion.

Comparison of Observations and Calculations

A comparison of these qualitative observations with the theory outlined previously can be carried out by considering the conductivity behavior in terms of the following equation derived from equations (14) and (18):

$$\ln\sigma(x) = [\ln\sigma' + \frac{S(x)}{R}] - \frac{E(x)}{RT} \tag{22}$$

In comparing theory with experimental data in terms of these equations two cases are immediately apparent.

Case 1. The temperature derivative of J, $\left(\frac{\partial J}{\partial T}\right)_{P,x}$ is assumed to be negligible.

In this case, $E_a(x)$ can be calcualted and $\ln\sigma_o(x)$ is linear, with the values of $\ln\sigma_A$ and $\ln\sigma_B$ being determined by conductivity measurements of the end membered glasses (x = 0 or 1) in the mixed alkali glass series. This case provides a zero parameter theory in which the properties of the mixture can be calculated based on measurements of the properties of the end membered glasses in the series.

Case 2. The temperature derivative of J, $\left(\frac{\partial J}{\partial T}\right)_{P,x}$, is not negligible.

In this case, a least squares fit of the data to equation (18) determines $J-T\left(\frac{\partial J}{\partial T}\right)_{P,x}$. By calculating J as in Case 1, $\left(\frac{\partial J}{\partial T}\right)_{P,x}$ can be determined. This case provides for a one parameter theory in which the fitting parameter is $\left(\frac{\partial J}{\partial T}\right)_{P,x}$. Now if $\left(\frac{\partial J}{\partial T}\right)_{P,x}$ happens to be negative, the maximum in $E_a(x)$ will be larger and a maximum will appear in $\ln\sigma_o(x)$. As will be shown, $(\partial J/\partial T)_{P,x}$ as determined by this method is negative for all systems examined so far, and the result is that the energies and the pre-exponential factors both fit the data very well.

The results of the calculations using this model in Cases 1 and 2 for several mixed alkali glass systems are summarized in Table I and some representative results are plotted in Figures 1 through 4.

Some Observations About the Non-Linearities

Equation (22) is identical to equation (18) if we let

$$\ln\sigma_o(x) = \ln\sigma' + \frac{S(x)}{R} \tag{23}$$

where $\ln\sigma'$ corresponds to the constant term $\ln t_o$ of equation (14). If equation (22) is differentiated with respect to x and set equal to zero, it is found that the composition at which the minimum in conductivity occurs is given by

$$x_{\text{min, cond}} = \frac{\Delta G^\circ_A - \Delta G^\circ_B + J}{2J} \tag{24}$$

The maxima in E(x) and S(x) can be similarly determined and are given by the expressions

$$x_{\text{max},E} = \frac{\Delta E^\circ_A - \Delta E^\circ_B + J - T\left(\frac{\partial J}{\partial T}\right)_{P,x}}{2[J-T\left(\frac{\partial J}{\partial T}\right)_{P,x}]} \tag{25}$$

and

$$x_{max,S} = \frac{\Delta S^{\circ}_{A}-\Delta S^{\circ}_{B}\left(\frac{\partial J}{\partial T}\right)_{P,x}}{-2(\partial J/\partial T)_{P,x}} \qquad (26)$$

Equation (24) indicates that if J is positive, as it always is, a minimum in $\ln\sigma(x)$ will occur and that the position of the minimum will depend on the relative magnitude of $\Delta G^{\circ}_{A}-\Delta G^{\circ}_{B}$ with respect to J. If $\Delta G^{\circ}_{A}-\Delta G^{\circ}_{B}$ (which is proportional to $\ln\sigma_{A}-\ln\sigma_{B}$) is zero, the minimum will occur at $x = 0.5$. In those mixed alkali glass systems studied so far, it has been found that $\Delta G^{\circ}_{A}-\Delta G^{\circ}_{B}$ is positive and small relative to J so that the predicted minimum in conductivity is shifted to some composition $x > 0.5$.

In discussing the predictions of equations (25) and (26) with respect to the maxima in E(x) and S(x), it is useful to point out (see Table I) that the term $(\partial J/\partial T)_{P,x}$ is negative, as determined by experiment. This means that the term $J - T\left(\frac{\partial J}{\partial T}\right)_{P,x}$ of equation (25) is always positive and grater than J. Thus, the maximum in E(x) is determined by the relative magnitude of $\Delta E^{\circ}_{A}-\Delta E^{\circ}_{B}$ with respect to $J - T\left(\frac{\partial J}{\partial T}\right)_{P,x}$. If $\Delta E^{\circ}_{A}-\Delta E^{\circ}_{B}$ is zero, the maximum will occur at $x = 0.5$ and if $\Delta E^{\circ}_{A}-\Delta E^{\circ}_{B}$ is greater than zero, the maximum will occur at $x > 0.5$. The energy difference $\Delta E^{\circ}_{A}-\Delta E^{\circ}_{B}$ is usually found to be positive and small compared to $J - T\left(\frac{\partial J}{\partial T}\right)_{P,x}$ and the predicted maximum in E(x) is shifted to some composition $x > .5$.

The maximum in S(x) is expressed by equation (26) and is determined by the relative magnitude of the terms $\Delta S^{\circ}_{A}-\Delta S^{\circ}_{B}$ (which is proportional to $(\ln\sigma^{\circ}_{A}-\ln\sigma^{\circ}_{B})$ and $(\partial J/\partial T)_{P,x}$. It has been observed that the relative magnitude of these terms does not follow a regular pattern, and in some cases the maximum predicted by equation (26) is not in the composition range $0 < x < 1$. If $(\partial J/\partial T)_{P,x}$ is zero, there is no maximum and $\ln\sigma_{a}(x)$ is simply a straight line.

TABLE I

X	Log σ obs.	Log σ_o obs.	Ea obs.	Log σ calc.	Ea calc $\partial J'/\partial T = 0$	$\frac{\partial J'}{\partial T}$ 0, for best Ea fit	Log σ_o calc. $\partial J'/\partial T$ 0	Ea calc. $\partial J'/\partial T$ 0	
x $Cs_2O\cdot(1-x)Na_2O\cdot 5SiO_2$, Ref. 23									
0	- 6.0	4.2	17.0	- 6.0	17.0		4.2	17.0	r_L = 4.2 Å
0.1	- 7.1	3.8	19.0	- 7.2	19.6		5.2	20.6	
0.2	- 8.0	3.9	21.0	- 8.3	21.6		5.8	23.4	r_S = 3.3 Å
0.3	- 9.0	3.7	23.0	- 9.0	23.2		6.3	25.5	ν_L = 89 cm^{-1}
0.4	- 9.5	4.7	25.0	- 9.6	24.2		6.5	26.9	
0.5	-10.4	4.7	27.0	- 9.9	24.8	-.023	6.4	27.5	ν_S = 256cm^{-1}
0.6	-11.0	5.5	29.0	-10.0	24.8		6.2	27.5	
0.7	-10.8	4.9	28.0	- 9.8	24.4		5.7	26.7	
0.8	-10.0	3.0	24.5	- 9.5	23.4		5.0	25.2	
0.9	- 9.0	2.1	21.5	- 8.8	22.0		4.0	23.0	
1.0	- 8.0	2.8	20.0	- 8.0	20.0		2.8	20.0	
x $Cs_2O\cdot(1-x)Rb_2O\cdot 6.7SiO_2$, Ref. 3									
0	- 5.5	4.6	21.4	- 5.5	21.4		4.6	21.4	r_L = 4.2 Å
0.33	- 6.3	8.8	28.9	- 6.3	23.9		8.7	28.9	
0.50	- 6.5	9.3	30.1	- 6.5	24.3	-.036	9.3	30.0	r_S = 3.69 Å
0.67	- 6.4	8.7	29.0	- 6.4	24.2		8.8	29.2	ν_L = 95 cm^{-1}
1.0	- 5.8	4.8	22.5	- 5.8	22.5		4.8	22.5	
									ν_S = 131 cm^{-1}

TABLE I (Continued)

X	Log σ obs.	Log σ_o obs.	Ea obs.	Log σ calc.	Ea calc. $\partial J'/\partial T = 0$	$\frac{\partial J'}{\partial T}$ for best Ea fit	Log σ_o calc. $\partial J'/\partial T$ 0	Ea calc. $\partial J'/\partial T$ 0	
				x $Cs_2O\cdot(1-x)K_2O\cdot6.7SiO_2$, Ref. 13					
0	-5.0	4.2	19.5	-5.0	19.5		4.2	19.5	r_L = 4.2 Å
0.33	-6.5	9.6	30.5	-6.5	24.1		9.4	30.3	r_S = 3.51 Å
0.50	-7.1	9.9	32.5	-6.8	25.1	-.045	10.1	32.1	ν_L = 95 cm^{-1}
0.67	-6.8	9.4	31.1	-6.8	25.2		9.6	31.3	
1.00	-5.9	5.0	22.8	-5.8	22.5		4.8	22.5	ν_S = 194 cm^{-1}
				x $Cs_2O\cdot(1-x)Na_2O\cdot6.7SiO_2$, Ref. 13					
0	-4.8	3.1	17.5	-4.8	17.5		3.1	17.5	r_L = 4.2 Å
0.33	-6.9	9.2	31.1	-7.3	25.3		8.3	31.0	r_S = 3.3 Å
0.50	-7.4	10.3	33.9	-7.7	26.9	-.042	9.2	33.4	ν_L = 95 cm^{-1}
0.67	-7.1	9.4	31.9	-7.6	27.0		8.9	32.7	
1.0	-5.8	4.8	22.5	-5.8	22.5		4.8	22.5	ν_S = 256 cm^{-1}
				x $Cs_2O\cdot(1-x)Li_2O\cdot6.7SiO_2$, Ref. 13					
0	-4.2	3.1	15.8	-4.2	15.8		3.1	15.8	r_L = 4.2 Å
0.33	-7.3	11.4	35.0	-7.3	28.4		8.4	34.2	r_S = 3.02 Å
0.50	-7.6	12.5	37.2	-7.6	30.9	-.042	9.3	37.5	
0.67	-7.8	11.2	36.1	-7.8	30.7		8.9	36.5	ν_L = 95 cm^{-1}
1.0	-5.8	4.8	22.5	-5.8	22.5		4.8	22.5	ν_S = 483 cm^{-1}

Figure 1: Observed and calculated (case 1) Log σ and E_a vs. x for the mixed alkali glass system $x\ Cs_2O \cdot (1-x)Na_2 \cdot O \cdot 6 \cdot 7SiO_2$. Data from Ref. 3.

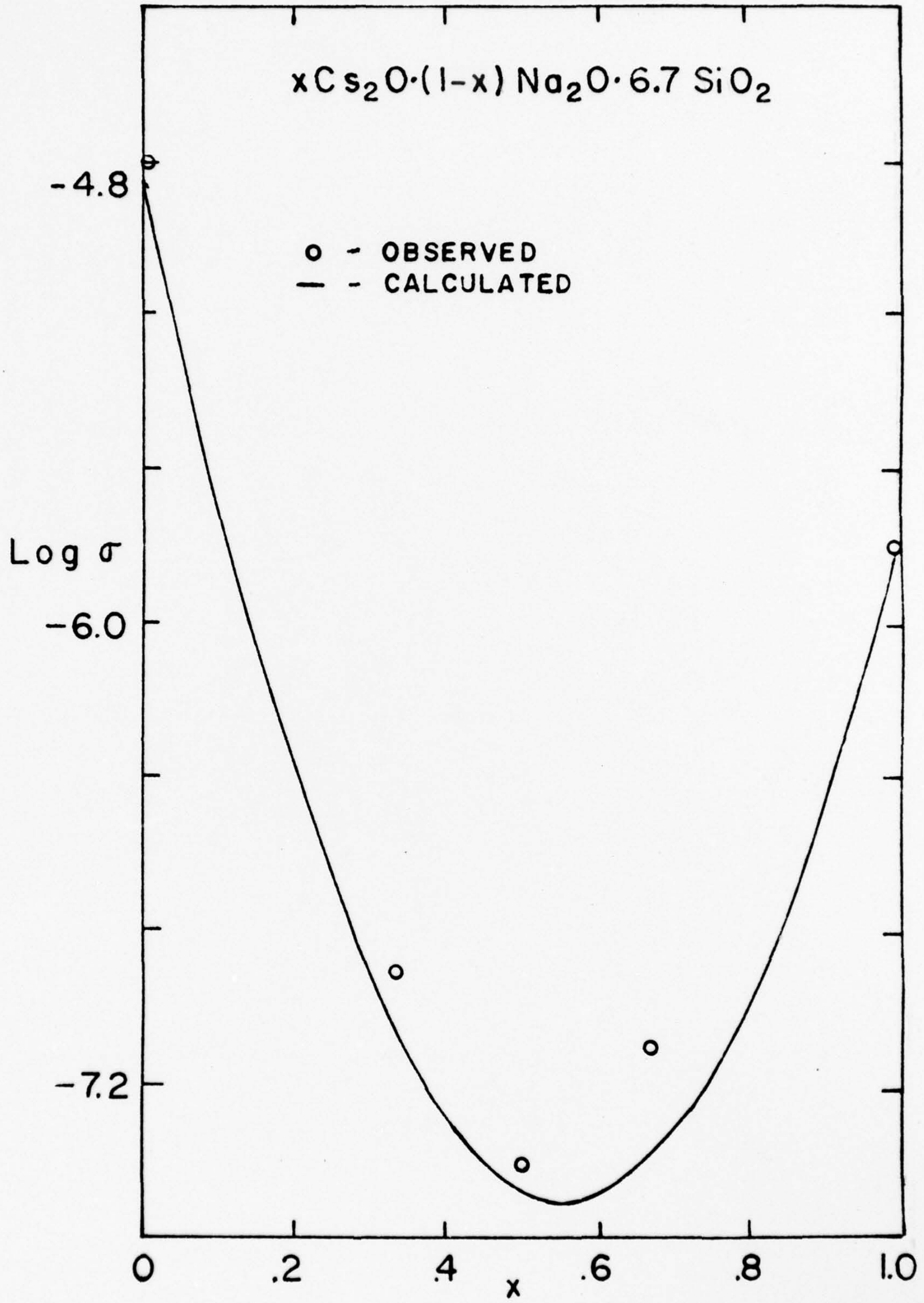

$xCs_2O\cdot(1-x)Na_2O\cdot 6.7\ SiO_2$
o - OBSERVED
— - CALCULATED
Log σ
-4.8
-6.0
-7.2
0
.2
.4
.6
.8
1.0
x

Figure 2: Observed and calculated (case 1) Log σ and E_a vs. x for the mixed alkali glass system x $Cs_2O \cdot (1-x) Rb_2O \cdot 6 \cdot 7\ SiO_2$. Data from Ref. 3.

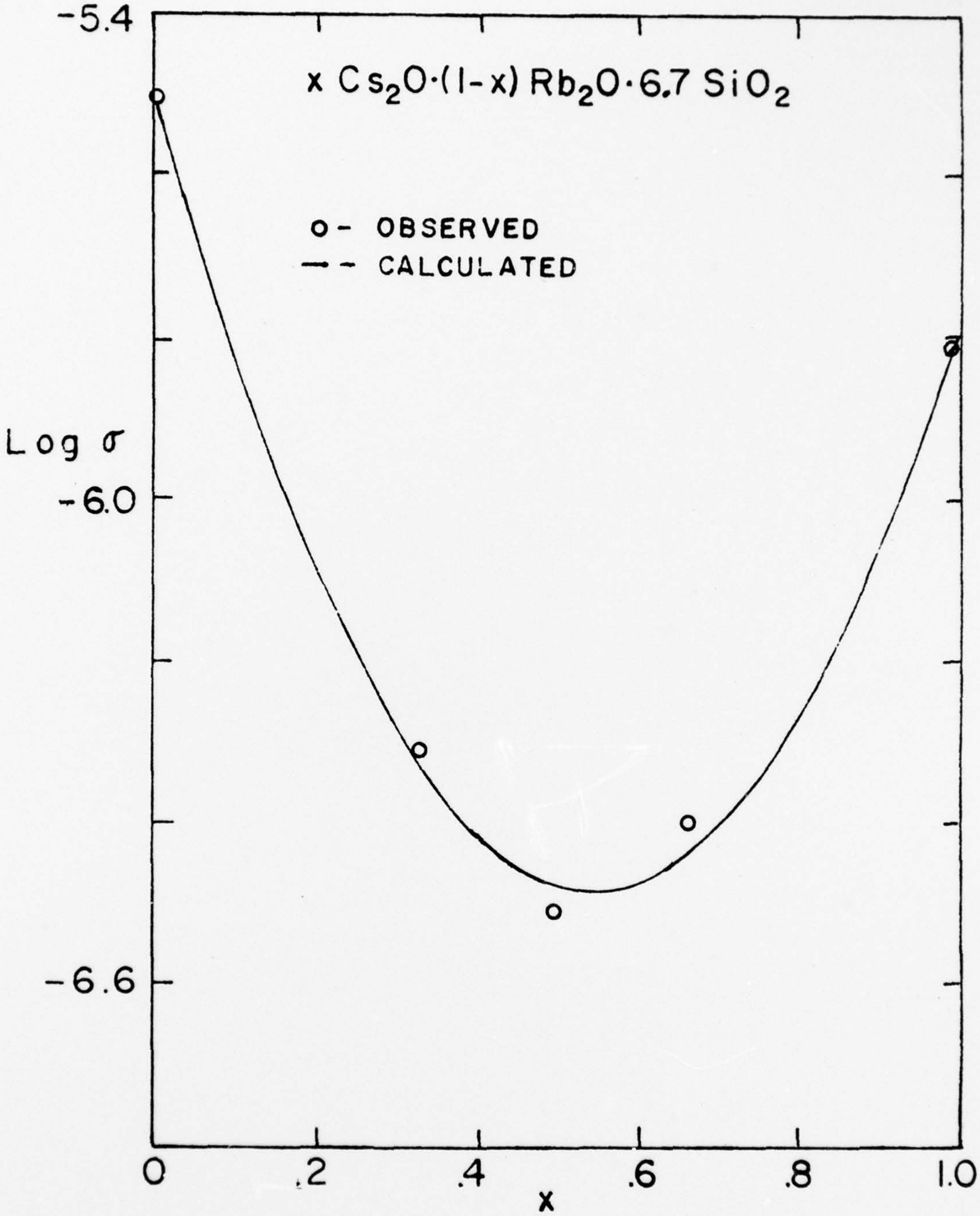

-5.4
-6.0
-6.6
Log σ
x $Cs_2O\cdot(1-x)Rb_2O\cdot6.7SiO_2$
o - OBSERVED
— - CALCULATED
0
.2
.4
.6
.8
1.0
x

Figure 3: Observed and calculated (case 2 with $\left(\frac{\partial J}{\partial T}\right)_{P,x} = 0$) x for the mixed alkali glass system x $Cs_2O\cdot(1-x)$ $Na_2O\cdot 5SiO_2$. Data from Ref. 23.

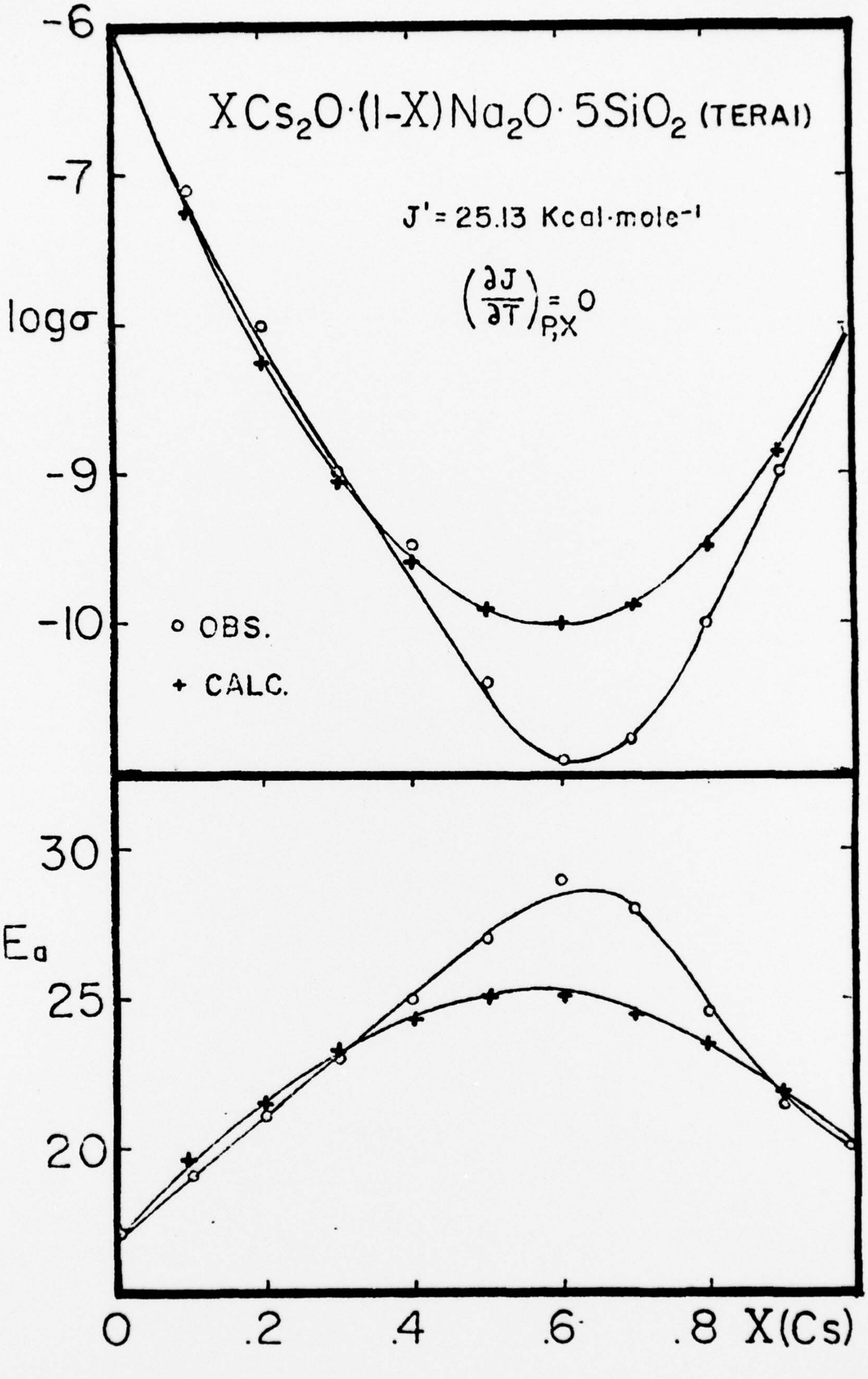
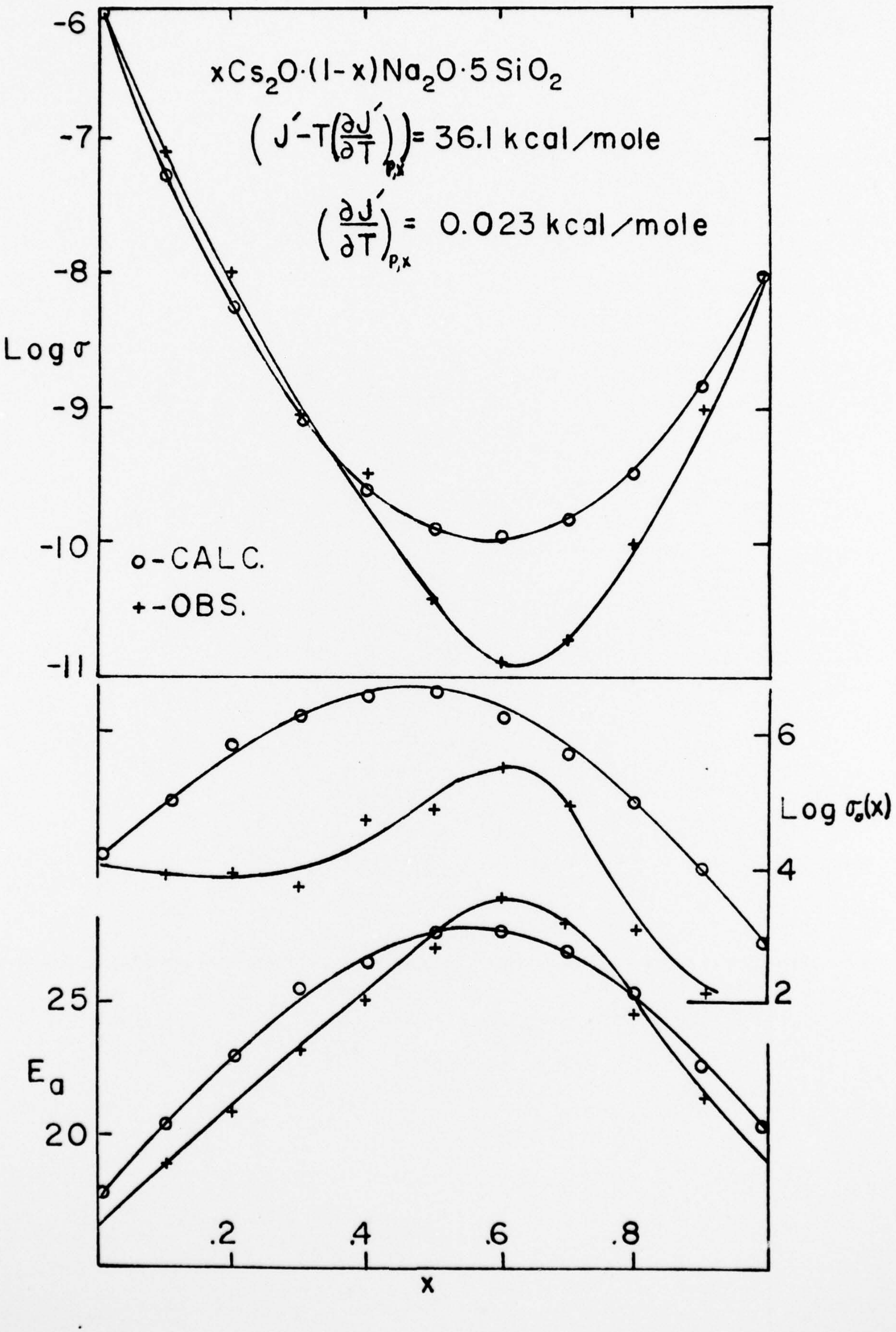

XCs₂O·(1-X)Na₂O·5SiO₂ (TERAI)
J' = 25.13 Kcal·mole⁻¹
(∂J/∂T)P,X = 0
○ OBS.
+ CALC.
log σ
-6
-7
-9
-10
Ea
30
25
20
0
.2
.4
.6
.8
X(Cs)

Figure 4: Observed and calculated (case 2, with $\left(\frac{\partial J}{\partial T}\right)_{P,x} \neq 0$) for the mixed alkali glass system x $Cs_2O \cdot (1-x)$ $Na_2O \cdot 5SiO_2$. Data from Ref.


$xCs_2O\cdot(1-x)Na_2O\cdot5SiO_2$
$\left(J' - T\left(\frac{\partial J'}{\partial T}\right)_{P,x}\right) = 36.1$ kcal/mole
$\left(\frac{\partial J'}{\partial T}\right)_{P,x} = 0.023$ kcal/mole
o-CALC.
+-OBS.
Log σ
-6
-7
-8
-9
-10
-11
Log $\sigma_0(x)$
6
4
2
E_a
25
20
.2
.4
.6
.8
x

Conclusions

The use of the inherently cooperative form of the expression for the activation of the transport processes, together with the introduction of the regular solution model for the composition dependence of the exponential in that expression provides a basis for understanding the non-linearities known as mixed alkali effects in binary ionic oxide glasses. In order to estimate the magnitudes of the parameter that expresses the non-ideality inherent in regular solutions, a molecular model has been introduced, which yields values of the right order of magnitude. Within this framework the variations in the experimentally derived exponential and pre-exponential terms can be understood.

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