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Abstract

We have established for alkali ions in oxide glasses a strong correlation between the fractional (Kohlrausch) exponent β in the conductivity relaxation function, $\exp[-(t/\tau^*)^\beta]$, and the activation energy E^* of τ^* and σ when varying the composition of oxide glass formers and the alkali ions while holding the alkali-ion concentration constant. An even stronger correlation of the trends in β and the product βE^* is found. These correlations were expected conceptually by the coupling model for conductivity relaxation, and the latter was the motivation behind the present undertaking of the establishment of the correlation from experimental data. The glass-forming oxides considered include P_2O_5 , SiO_2 , B_2O_3 , Al_2O_3 - B_2O_3 , GeO_2 , and Al_2O_3 - GeO_2 . In all, some 89 different compositions were examined and the alkali oxides considered include Li_2O , Na_2O , K_2O , Rb_2O , and some of their binary mixtures. The correlation will have a bearing on the viability of theoretical models of conductivity relaxation.

Disciplines

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Comments

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Correlation between the activation enthalpy and Kohlrausch exponent for ionic conductivity in oxide glasses

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We have established for alkali ions in oxide glasses a strong correlation between the fractional (Kohlrausch) exponent β in the conductivity relaxation function, $\exp[-(t/\tau^*)^\beta]$, and the activation energy E_a^* of τ^* and σ when varying the composition of oxide glass formers and the alkali ions while holding the alkali-ion concentration constant. An even stronger correlation of the trends in β and the product βE_a^* is found. These correlations were expected conceptually by the coupling model for conductivity relaxation, and the latter was the motivation behind the present undertaking of the establishment of the correlation from experimental data. The glass-forming oxides considered include P_2O_5 , SiO_2 , B_2O_3 , Al_2O_3 - B_2O_3 , GeO_2 , and Al_2O_3 - GeO_2 . In all, some 89 different compositions were examined and the alkali oxides considered include Li_2O , Na_2O , K_2O , Rb_2O , and some of their binary mixtures. The correlation will have a bearing on the viability of theoretical models of conductivity relaxation.

I. INTRODUCTION

The first observation that a correlation exists between the activation enthalpy E_a^* of dc conductivity and the fractional (Kohlrausch) exponent β ($\equiv 1-n$) in the electric-field-relaxation function,

$$\phi(t) = \exp[-(t/\tau^*)^\beta], \quad (1)$$

used to describe conductivity relaxation was made by Martin and Angell¹ in lithium phosphate glasses, $xLi_2O + (1-x)P_2O_5$. Over the composition range x of 37% to 62%, β decreases from 0.60 to 0.49, while E_a^* decreases also from 97.2 to 55.9 kJ/mol. This same correlation of the trends in β and E_a^* with alkali oxide concentration has been seen also in Na aluminoborate glasses by Martin,² and also in sodium and rubidium germanate glasses, $xNa_2O + (1-x)GeO_2$ and $xRb_2O + (1-x)GeO_2$, as well as in mixed alkali aluminogermanate glasses, $xNa_2O + yRb_2O + zAl_2O_3 + (1-x-y-z)GeO_2$, by Ngai *et al.*^{3,4}

In all of these studies, however, it was found that the correlation in the trends of the conductivity activation energy E_a^* and β were not perfect. A better correlation was obtained in the trends of β and another activation energy, E_a , defined to be the product

$$E_a = \beta E_a^*. \quad (2)$$

This quantity E_a in a theoretical model of conductivity relaxation (referred to as the coupling model) is identified with the microscopic energy barrier.³⁻⁵ The latter is to be obtained from a consideration of the energetics of cation-conduction process such as the Anderson-Stuart⁶ model or the weak-electrolyte model.⁷

Taking advantage of the conductivity-relaxation data available for a large number of alkali and mixed alkali aluminogermanate glasses^{8,9} with different combinations of x , y , and z , the trends of β and E_a^* have been compared also upon varying the composition of the glass formers (i.e., $[Al_2O_3]$ to $[GeO_2]$ ratio) while keeping the alkali mole fraction constant.^{3,4} For example, in $xNa_2O + yAl_2O_3 + (1-x-y)GeO_2$, and in $xRb_2O + yAl_2O_3 + (1-x-y)GeO_2$ systems, upon varying the $[Al_2O_3]/[GeO_2]$ ratio while maintaining the alkali oxide mole percent constant,^{3,4} again we have found the correlation of the trends in β and E_a^* . Both decrease with increasing $[Al_2O_3]/[GeO_2]$ ratio (see Tables III and IV of Ref. 3). The same correlation is also found in mixed alkali aluminogermanate glasses upon keeping the sum of the Na_2O and the Rb_2O mole fractions constant.⁴ It is worthwhile to emphasize the difference between the case of changing alkali mole percent in the same class of oxide glasses^{1,2} and the case of varying the composition of the oxide glass formers while keeping the alkali oxide mole percent constant as discussed here. In varying alkali oxide mole percent in the same class of oxide glasses as $xLi_2O + (1-x)B_2O_3$, both the activation energy as well as the proximity of stable cation sites are altered. On the other hand, varying both the alkali oxide and the glass-network former while maintaining the total alkali oxide mole percent constant, the proximity of stable cation sites remains unchanged within slight variations in density. The only change is in the activation barrier energy.

The current view^{1-4,10,11} of the origin of the Kohlrausch relaxation function and its departure from the linear exponential [as measured by n ($\equiv 1-\beta$)] is from cooperation between alkali cations in conductivity relaxation. Therefore, an increase of concentration of al-

kali ions enhances cooperation and increases n , or decreases β . The model analysis of the energetics of the cation-conduction process by Martin and Angell¹ clearly indicates that increasing site proximity also causes decreasing total activation energy. Thus the observed correlation of the trends of decreases in both β and E_a^* with increasing alkali oxide mole percent may be the natural consequence of the combination of two inseparable and concomitant factors, namely increasing cooperativity with cation-site proximity and decreasing conduction-energy barrier.

From this discussion, the fact that the correlation of the trends in β and E_a^* continued to be observed when varying composition of oxide glass formers (e.g., $[\text{Al}_2\text{O}_3]/[\text{GeO}_2]$ ratio in aluminogermanate glasses) while keeping the total alkali oxide mole percent constant^{3,4} presents a challenge for physical interpretation. This correlation is expected from the coupling model^{12,13} on heuristic grounds, and that is the reason it was examined in the first place. With the alkali-ion concentration being kept constant, we do not expect that, at least in the first approximation, the degree of cooperation (as measured by $1-\beta$ or n) coming from cation-site proximity to change upon varying the composition of glass formers. On the other hand, the microscopic barrier activation energy of the cation E_a and the corresponding bulk conductivity activation energy E_a^* can be changed by this composition variation. If, to a good approximation, this is the only effect there is, then changes in β or the degree of cooperation can be considered to be caused solely by changes in microscopic barrier activation energy. The effect the latter has on the cooperation of the cation motions must be rather subtle. Now it becomes clear that the observed correlation of decrease in β and E_a^* or E_a poses a challenging empirical fact to explain. We restate this empirical result more directly as follows: A decrease in the cation barrier activation energy by varying the composition of glass formers while keeping the cation concentration constant has the effect of decreasing the Kohlrausch exponent β of conductivity relaxation.

An initial attempt has been made to explain this by the coupling model of relaxation.¹²⁻¹⁴ Basically the idea is that higher barrier energies increase the relative importance of the one-particle terms compared with the many-particle terms of the classical Hamiltonian of the ions in a glass. The many-particle terms give rise to correlations between ions. Their decrease in importance compared with one-particle terms lessens the effect of cooperation between ions in conductivity relaxation and results in an increase of β . If cooperation is cast in the phase-space dynamical-constraint formulation of the coupling model,¹³ and if higher barrier energy corresponds to increased confinement in the phase space of each ion, then constraints between the phase-space variables of the ions are effectively reduced. An entropy reformulation^{12,14} of the constraint-dynamics model¹³ and an established entropy inequality have been used to derive the correlation of trends,

$$\beta < \beta' \text{ if } E_a < E_a' . \quad (3)$$

Here, (β, E_a) and (β', E_a') are two pairs of Kohlrausch ex-

ponents and barrier activation energies for two different compositions of glass formers having the same alkali oxide mole fraction.

Previously, in the aluminogermanate glasses the glass composition was varied by changing the $[\text{Al}_2\text{O}_3]/[\text{GeO}_2]$ ratio.^{3,4} The change in composition is controlled and its effect on the glass structure known. It is a rich system to employ for the establishment of the correlation. Success in this system has given us sufficient confidence to embark on a much bolder endeavor: to explore the extent to which a "universal" correlation exists between β and E_a or E_a^* at a constant concentration of alkali ions for glassy ionic conduction. Due to the limited range of available data, a condition which is probably caused by the fact that one parameter, β , comes from ac-conductivity measurements and the other, E_a^* , comes from dc-conductivity measurements, the "universal" nature of the correlation can only be explored for the more widely known and, hence, studied, glass-forming systems. For the present contribution these will consist of phosphate, silicate, borate, and aluminoborate glasses with various ratios of $[\text{Al}_2\text{O}_3]/[\text{B}_2\text{O}_3]$, germanate, and finally aluminogermanate with various ratios of $[\text{Al}_2\text{O}_3]/[\text{GeO}_2]$. We also include halogenated borate glasses. The total alkali oxide mole percent is fixed, while the alkali-cation type or types for mixed alkalis varied from Li, to Na, to K, and to Rb. Variation of cation type also modifies the cation barrier energy E_a because the energetics depend on cation size. The principal effect of varying cation type or types on the Kohlrausch exponent β is through the change in barrier energy E_a if the total alkali oxide mole percent is kept constant.

II. COLLECTION OF EXPERIMENTAL DATA

The conductivity-relaxation data sets for oxide glasses have been assembled, each of which provides both the value of the Kohlrausch exponent β of the conductivity-relaxation function and the conductivity activation energy E_a^* . Some are published data and some are not. Values of β for some glasses were determined previously by us either separately in studies of conductivity relaxation or in collaboration with others.^{1-5,11,15} The remainder are taken either from published data¹⁶ or determined specifically for this work by fitting the electric modulus data^{8,17} with theoretical predictions based on the Kohlrausch relaxation function. The alkali oxides include Li_2O , Na_2O , K_2O , and Rb_2O and some of their binary mixtures. The glass-forming oxides include P_2O_5 , SiO_2 , B_2O_3 , $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, GeO_2 , and $\text{Al}_2\text{O}_3\text{-GeO}_2$. Some glasses are halogenated, i.e., containing alkali halides.

The experimental data are presented in Table I. For each row, the glass composition, the total alkali oxide mole fraction, the Kohlrausch exponent β (presented also in the form of $1-\beta$, which is the coupling parameter n in the coupling model), the conductivity activation energy E_a^* , and the quantity βE_a^* (which, according to the coupling model, is the microscopic energy barrier, E_a , to migration of the cation) has been specified. The identification of βE_a^* with the microscopic energy barrier was supported by nuclear-magnetic-resonance measure-

TABLE I. Conductivity relaxation data of alkali oxide glasses.

Glass composition (class number), [reference]	Total alkali oxide mol fraction c	Kohlrausch exponent β	Coupling parameter n	Conductivity activation energy, E_a^* (kJ/mol)	E_a ($\equiv \beta E_a^*$) (kJ/mol)
$x\text{Li}_2\text{O} + (1-x)\text{P}_2\text{O}_5$ (1),[1]	0.368	0.600	0.400	97.19	58.31
	0.407	0.591	0.409	88.64	52.39
	0.450	0.561	0.439	75.45	42.32
	0.500	0.577	0.423	68.99	39.81
	0.550	0.538	0.462	63.44	34.13
	0.600	0.507	0.493	59.31	30.07
	0.625	0.492	0.508	55.87	24.49
$x\text{Na}_2\text{O} + (1-x)\text{P}_2\text{O}_5$ (2),[10]	0.50	0.600	0.400	68.49	41.09
	0.55	0.600	0.400	65.69	39.41
	0.60	0.549	0.451	61.39	33.70
$x\text{Li}_2\text{O} + (1-x)\text{B}_2\text{O}_3$ (3),[17,21]	0.25	0.52–0.57	0.48–0.43	83.40	45.04
$0.25\text{Na}_2\text{O} + 0.75\text{B}_2\text{O}_3$ (4),[22]	0.25	0.55	0.45	83.40	45.87
$0.267[0.49\text{Li}_2\text{O} + 0.51\text{Na}_2\text{O}]$ $+ 0.733\text{B}_2\text{O}_3$ (5),[11]	0.267	0.55	0.45	110.1	60.56
$0.2[(\text{Li}_2\text{O})_{0.3} + (\text{Na}_2\text{O})_{0.7}]$ $+ 0.8\text{B}_2\text{O}_3$ (5),[17]	0.20	0.61	0.37	116.0	70.76
$0.25[0.1\text{LiF} + 0.9\text{Li}_2\text{O}]$ $+ 0.75\text{B}_2\text{O}_3$ (6),[22]	0.25	0.59	0.41	87.84	51.83
$0.25[0.1\text{LiF} + 0.45\text{Na}_2\text{O}]$ $+ 0.45\text{Li}_2\text{O} + 0.75\text{B}_2\text{O}_3$ (6),[22]	0.25	0.68	0.32	119.50	81.26
$x\text{Li}_2\text{O} + (1-x)[0.87\text{B}_2\text{O}_3:$ $0.13\text{Al}_2\text{O}_3]$ (7),[10]	0.30	0.512	0.488	73.10	37.43
	0.35	0.490	0.510	66.99	32.83
	0.40	0.501	0.499	61.98	31.05
	0.45	0.468	0.532	59.34	27.77
$x\text{Na}_2\text{O} + (1-x)[0.87\text{B}_2\text{O}_3:$ $0.13\text{Al}_2\text{O}_3]$ (8),[2,10]	0.20	0.527	0.473	81.0	46.69
	0.25	0.517	0.483	77.2	39.91
	0.30	0.507	0.493	71.1	36.05
	0.35	0.543	0.457	65.2	35.4
	0.40	0.538	0.462	60.4	32.50
	0.425	0.517	0.483	60.2	31.12
	0.45	0.507	0.493	56.1	28.44
	0.55	0.497	0.503	55.9	27.78
	0.575	0.485	0.515	54.9	26.6
	0.60	0.574	0.426	59.0	33.83
$x\text{Na}_2\text{O} + (1-x)[0.80\text{B}_2\text{O}_3:$ $0.20\text{Al}_2\text{O}_3]$ (9),[2,10]	0.30	0.527	0.473	71.8	37.84
	0.35	0.507	0.493	66.0	33.46
	0.40	0.507	0.493	62.2	31.54
	0.425	0.511	0.489	59.9	30.6
	0.50	0.543	0.457	55.8	30.30
	0.525	0.527	0.473	56.5	29.78
	0.55	0.549	0.451	58.2	31.95
	0.575	0.583	0.417	60.1	35.04
	0.60	0.610	0.390	62.0	37.80

TABLE I. (Continued).

Glass composition (class number), [reference]	Total alkali oxide mol fraction c	Kohlrausch exponent β	Coupling parameter n	Conductivity activation energy E_a^* (kJ/mol)	E_a ($\equiv \beta E_a^*$) (kJ/mol)		
$x\text{Na}_2\text{O} + (1-x)\text{SiO}_2$ (10), [16, 19, 20, 23]	0.0006	1.0	0.0	125.5	125.5		
	0.25	0.48–0.512	0.52–0.488	60.05	28.8–30.74		
		anneal at 513.4 °C					
		0.469–0.514 annealed at 467 °C	0.531–0.486	59.80	29.06–31.75		
$x\text{K}_2\text{O} + (1-x)\text{SiO}_2$ (11), [16]	0.25	0.474–0.534 rate cooled	0.526–0.466 rate cooled	59.63	27.79–31.37		
		0.487–0.527	0.513–0.473	60.93	28.82–31.25		
		0.476–0.548	0.524–0.452	61.10	27.62–32.02		
$x\text{K}_2\text{O} + (1-x)\text{SiO}_2$ (11), [16]	0.25	0.472–0.543	0.527–0.457	61.43	28.07–32.37		
$x[0.5\text{Na}_2\text{O} + 0.5\text{K}_2\text{O}] + (1-x)\text{SiO}_2$ (12), [24]	0.25	0.535	0.465	101.34	54.2		
$x\text{Na}_2\text{O} + (1-x)\text{GeO}_2$ (13), [3–5, 8, 9]	0.0006	1.0	0.0	105.2	105.2		
	0.012	0.60	0.40	95.56	57.33		
	0.049	0.52	0.48	96.52	50.19		
	0.0984	0.52	0.48	98.45	51.20		
	0.1495	0.56	0.44	88.80	49.73		
	0.2894	0.55	0.45	62.73	32.81		
$x\text{Rb}_2\text{O} + (1-x)\text{GeO}_2$ (14), [4]	0.049	0.90	0.10	138.03	124.52		
	0.0124	0.85	0.15	135.13	114.86		
	0.0883	0.72	0.28	140.83	101.35		
	0.151	0.685	0.315	99.42	68.1		
	0.219	0.615	0.385	77.22	47.5		
	0.291	0.61	0.39	70.46	43.00		
$x\text{Na}_2\text{O} + y\text{Rb}_2\text{O} + (1-x-y)\text{GeO}_2$ (15), [4]	15 A3	0.15	0.55	0.45	110.04	60.81	
	15 A5	0.15	0.58	0.42	118.72	68.53	
	15 A7	0.15	0.56	0.44	124.52	69.50	
	10 A7	0.10	0.55	0.45	125.48	69.50	
	10 A5	0.10	0.64	0.34	131.27	86.87	
	10 A3	0.10	0.54	0.46	111.00	59.85	
	20 C7	0.10	0.53	0.47	105.21	55.98	
	$x\text{Na}_2\text{O} + y\text{Al}_2\text{O}_3 + (1-x-y)\text{GeO}_2$ (16), [4, 9]	$y = 0.0488$	0.0551	0.46	0.54	82.05	37.74
		$y = 0.0324$	0.1586	0.53	0.47	86.87	46.04
$y = 0.0511$		0.1466	0.50	0.50	83.98	41.99	
$y = 0.141$		0.1547	0.48	0.52	71.43	34.29	
$y = 0.0030$		0.1868	0.57	0.43	80.12	45.67	
$y = 0.072$		0.2141	0.55	0.45	74.32	40.88	
$y = 0.1877$		0.2053	0.47	0.53	62.74	29.49	

TABLE I. (Continued).

Glass composition (class number), [reference]	Total alkali oxide mol fraction c	Kohlrausch exponent β	Coupling parameter n	Conductivity activation energy E_a^* (kJ/mol)	E_a ($\equiv \beta E_a^*$) (kJ/mol)
$x\text{Na}_2\text{O} + y\text{Rb}_2\text{O} + z\text{Al}_2\text{O}_3$ $+ (1-x-y-z)\text{GeO}_2$ (17), [4,9]					
30B7	0.225	0.60	0.40	114.86	68.9
30B3	0.225	0.55	0.45	102.3	55.98
10B7	0.075	0.60	0.40	133.20	80.12
10C5	0.050	0.54	0.46	94.59	51.16
10C3	0.050	0.50	0.50	88.80	44.40
30C7	0.15	0.53	0.47	95.56	51.16
30C3	0.15	0.47	0.53	83.97	39.57
20B7	0.15	0.54	0.46	127.41	68.53
20B3	0.15	0.50	0.50	112.93	56.95
20C7	0.10	0.53	0.47	105.21	55.98
20C10	0.0951	0.47	0.53	102.32	48.26
20C3	0.10	0.46	0.54	81.08	37.64
20B5	0.15	0.54	0.46	112.93	60.81
20C5	0.10	0.57	0.43	93.63	53.09
10B3	0.075	0.50	0.50	99.42	50.19
$x\text{Rb}_2\text{O} + y\text{Al}_2\text{O}_3$ $+ (1-x-y)\text{GeO}_2$ (18), [4]					
$y=0.0468$	0.0468	0.57	0.43	111.00	63.27
$y=0.0925$	0.927	0.47	0.53	102.3	48.10
$y=0.15$	0.15	0.53	0.47	82.05	43.50

ments.⁵ The Kohlrausch exponent deduced by fitting the experimental data is often slightly temperature dependent. The range of β is given whenever available. We have given a class number to all glasses having identical alkali oxide or mixed alkali oxides and glass former or formers, but different compositions. The sources of the data sets are indicated also. These data sets will be analyzed and examined for possible correlations in trends in the next section.

III. CORRELATIONS BETWEEN n AND E_a AT CONSTANT c

Consider a fixed value c of the alkali oxide or the total alkali oxides mole fraction. From the 18 classes of glasses given in Table I, the list of the glasses that have this value of c have been compiled. For each glass in this list, the coupling parameter n , the dc-conductivity activation energy E_a^* , and the quantity

$$E_a \equiv (1-n)E_a^* \quad (4)$$

are collected. The values of n and E_a (or E_a^*) in this list are examined for possible correlation. In some class there may be no glass that has the exact value c for the total alkali oxide mole percent. In this case, if data for

other values of c are available, the values of n , E_a , and E_a^* were determined by interpolation or extrapolation. In a few cases, if there is a glass with ion concentration sufficiently close to c and there is not sufficient data in the class to allow interpolation or extrapolation, n , E_a^* , and E_a are taken from the glass which is considered a member of the list. The data, after being reshuffled and reclassified according to c , are presented in the tables¹⁸ for $c=0.60, 0.55, 0.50, 0.45, 0.40, 0.35, 0.30, 0.25, 0.20, 0.15, 0.10, 0.075,$ and 0.050 . In the tables the data sets are arranged in order of decreasing E_a . An example is given as Table II here for $c=0.20$. By inspection, E_a^* and E_a are both found to decrease as n increases with very few exceptions. Henceforth, we shall refer to these results as correlations between n and E_a or E_a^* . Out of a total of 72 cases, there are only four violations. None of

TABLE II. Conductivity relaxation data of alkali oxide glasses having total alkali oxide mole fraction of $c=0.20$.

Class number	β	n	E_a^* (kJ/mol)	E_a (kJ/mol)
5	0.61	0.37	116.0	70.76
14	0.620	0.38	88.5	56.2
16	0.56	0.44	77.0	43.12
8	0.527	0.473	81.0	42.69
16	0.47	0.53	62.74	29.49

these four violations are serious enough to invalidate the overall correlations observed. The correlation of n with E_a is stronger than that between n and E_a^* . There are a few instances ($c=0.45, 0.30, 0.20$, and 0.05) where the correlation holds for n versus E_a , but is violated for n versus E_a^* . This feature was found before in an earlier work.⁴

The correlation between n and E_a at constant c is brought out clearly by plotting n versus E_a from the data in the tables collectively as in Fig. 1 with c as a parameter. The trend that n decreases with increasing E_a is evident for each c , although strictly there is no unique pattern. A unique pattern of the correlation between n and E_a for all c is not expected here because at a fixed concentration the data are collected over several different classes of oxide glasses, and a different combination of classes may be involved when going from one concentration to another. If we limit to concentrations each of which has the same combination of classes, the patterns of correlation can be quite similar. This is demonstrated in Fig. 2 for $c=0.05, 0.075$, and 0.10 , where data are taken exclusively from the germanate and aluminogermanate glasses. We have included in Fig. 1 the pure-exponential (i.e., $n=0$) conductivity-relaxation data for two extremely low alkali oxide glasses. An example is the $\text{Na}_2\text{O}+\text{SiO}_2$ glasses containing ppm-level amounts of Na_2O (Refs. 19 and 20) and another is $\text{Na}_2\text{O}+\text{GeO}_2$ glass containing 0.0006 mole fraction of Na_2O .⁸ In these low alkali oxide glasses, the effect of cooperation or coupling between alkali ions on their conductivity relaxations is absent, and hence n is always zero. The correlation be-

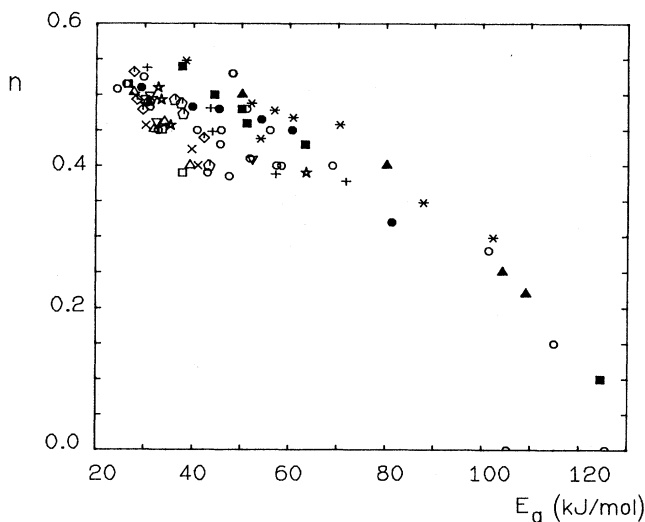


FIG. 1. A plot of the coupling parameter n vs E_a for alkali oxide glasses having total alkali oxide mole fraction of $c=0.05$ (■), 0.075 (▲), 0.10 (*), 0.20 (+), 0.25 (●), 0.30 (○), 0.35 (☆), 0.40 (▽), 0.45 (◇), 0.50 (×), 0.55 (△), 0.60 (□). [From Table II and 12 other tables in AIP documents (see Ref. 18).] Open circles are a collection of data from alkali oxide glasses in Table I that do not have c falling into the above 12 values. Two semi-circular points on the E_a axis are data from the very low alkali silicate and germanate glasses.

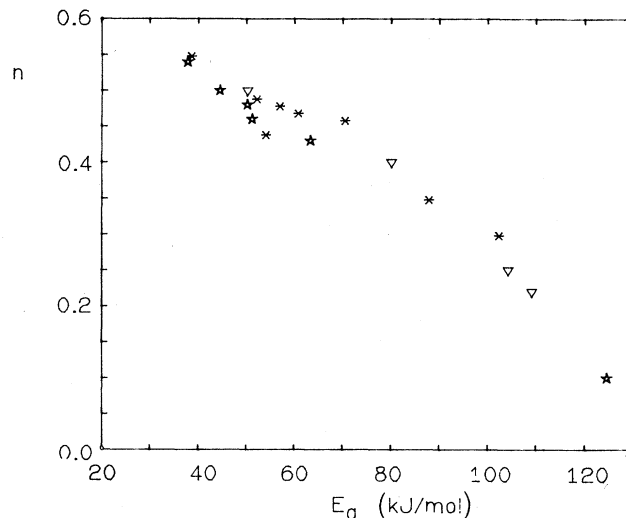


FIG. 2. A plot of n vs E_a for $c=0.05$ (☆), 0.075 (▽), and 0.10 (*). Here data are from the family of the alkali aluminogermanate glasses only.

tween n and E_a for low alkali oxide glasses with $c \ll 1$ does not exhibit the smooth decrease of n with increasing E_a established for the much higher alkali oxide glasses in Fig. 1. Instead, the correlation is trivially reduced to two points lying on the E_a axis in an n -versus- E_a plot (Fig. 1).

The lack of a closely similar pattern for all concentrations considered can be remedied somewhat if, for each c , we normalize E_a by E_{ac} , where E_{ac} is the value of E_a at which n assumes an arbitrary chosen constant value. The value of $E(c)$ varies with c and is approximately the same only for those concentrations which have a similar pattern (e.g., Fig. 2). In Fig. 3 the data are replotted in the format of n versus E_a/E_{ac} for ten values of c . Here we have chosen $n=0.39$ arbitrarily, and the values of E_{ac} obtained by interpolating the data points in Fig. 1 are, in

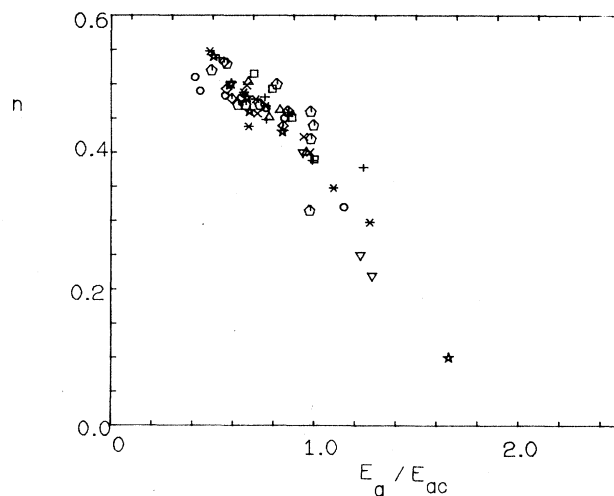


FIG. 3. A plot of n vs E_a/E_{ac} . Legends are the same as in Fig. 1. For values of E_{ac} , see text.

kJ/mol, 37.8 for $c=0.60$, 41.0 for $c=0.55$, 42.0 for $c=0.50$, 50.0 for $c=0.45$, 59.0 for $c=0.40$, 62.5 for $c=0.35$, 44.0 for $c=0.30$, 71.0 for $c=0.25$, 72.5 for $c=0.20$, and 81.0 for $c=1.0$. Even though there is still scattering, the pattern of the decrease of n with E_a for all concentrations becomes more similar to each other. Thus these figures have brought out vividly the essential results of this work: establishment of a correlation between the activation energy E_a and the Kohlrausch exponent β for ionic conductivity when varying over wide compositions of oxide glasses with different alkali ions and glass formers, while keeping the total concentration of alkali ions in each glass constant. As discussed in Sec. I, this correlation is consistent with what is expected from the coupling model.¹²⁻¹⁴ The theoretical treatment attempted so far is not quantitative. Nevertheless, it has led to the conclusion that this correlation in trends can be derived from the coupling model of conductivity relaxation of alkali ions in oxide glasses. Additional theoretical considerations based on other alternate formulations of the coupling model will be pursued in the future. Also, we shall investigate other models of conductivity relaxation to see if this correlation can be expected from them or not.

IV. SUMMARY AND CONCLUSIONS

In this work we have gathered all the conductivity-relaxation data of alkali ions in oxide glasses that we

know of, and have examined whether there is a correlation between the trends of the Kohlrausch exponent β and the conductivity barrier activation energy E_a^* upon varying the composition of the glass while keeping the total alkali ion mole percent constant. Both β and E_a^* are obtained from experimental data. We found that indeed there is a correlation between β and E_a^* . There is even a better correlation between β and the product $\beta E_a^* \equiv E_a$. This is a rather subtle correlation that may be used to discriminate between theoretical models of conductivity relaxation. The coupling model of conductivity relaxation predicts such a correlation and was the motivation for the undertaking of the present work to establish the correlation from available experimental data. Any serious theoretical model must be consistent with this observed correlation and be able to explain some other critical experimental facts established elsewhere.^{5,11,15} The latter include the anomalous isotope mass dependence of ionic conductivity,¹⁵ which so far can be explained by the coupling model only.

ACKNOWLEDGMENTS

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