Correlation between Ionic Radii and Cation Polarizability (Review)

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Abstract - The polarizability approach in the glasses has been detailed studied by V. Dimitrov and T. Komatsu. Here a review is taken on the basics of their literature values classifying on number of ions and there average values of cation polarizability given by Kordes and Pauling on the basis of a couple sets of free- ion polarizabilities.

***Key Words*:** Cation, Ionic radii, Cation polarizability.

1. INTRODUCTION

The estimation of free ion electronic polarizability of ions is a subject of the so-called polarizability approach in material science, which is well known especially in the field of glass science as done by Pauling [1], Born and Heisenberg [2], Fajans and Joos [3], J. Mayer and M. Mayer [4] and Kordes [5]. The purpose of the article is to consider the status of the polarizability approach in the glass science and to emphasize the role of the cation polarizability ions and ionic radii; helpful to the new researchers.

2. THEORY

Ions which are a part of the science subject Chemistry forms from atoms and electrons that have either gained or lost their weight by the removal or adding of one or more valence electrons which would create either positive or a negative charge. The ions with a negative charge are called anions and the ones with a positive charge are called cations. Since both of them have charges of opposing qualities, they get attracted to one another and thereby forming an ionic bond between them.

Cations are an atom or molecule that is positively charged ions. They are formed when a metal loses its electrons. They lose one or more than one electron and do not lose any protons. Therefore, they possess a net positive charge. Some examples of cations are Potassium (K^+), Calcium (Ca^{2+}), Boron (B^{3+}) and so on. The number of protons is more than the number of electrons in a cation.

Anions are an atom or molecule that is negatively charged ions. They are formed when non-metal gains the electrons. They gain one or more than one electron and do not lose any protons. Therefore, they possess a net negative charge. Some examples of anions are Iodide (I^-), Chlorine (Cl^-), Oxygen (O^{2-}), and so on. The number of electrons is more than the number of protons in an anion.

The ability of a cation to distort an anion is known as its polarization power and the tendency of the anion to become polarized by the cation is known as its polarizability. They have opposite polarizability trends. Anions are expected to be highly polarizable if they are large and cations are expected to have a high polarizing power when they are small and highly charged.

Pauling's values have been obtained on a theoretical treatment of the quadratic Stark effect by means of the following equation,

$$R = 0.0470n^4 (15n^2 + 21) \Sigma 1/(Z - S_R)^4$$

where R = ionic refraction, n = principal quantum number, Z = electron number and S_R = mole refraction screening constant.

On the other hand Kordes [5] has calculated the Free-ion polarizabilities on the basis of ionic radii by the equation,

$$[(R/0.603)^{1/3}]^{2/3} = kr_u = kr_z \, Z^{2//(n-1)}$$

where R = ionic refraction, r_u = univalent crystal radii,
r_z = actual crystal radii , n = Born repulsion exponent and
k = constant.

There are also values of cation polarizability reported from other sources [6,7]

3. RESULT AND DISCUSSION

3.1Group IA IB: In this review the average values of cation polarizability given by Kordes [α_i/A° (Kordes)] and Pauling [α_i/A° (Pauling)] are taken, with arranging the values in order of increasing cation polarizability.

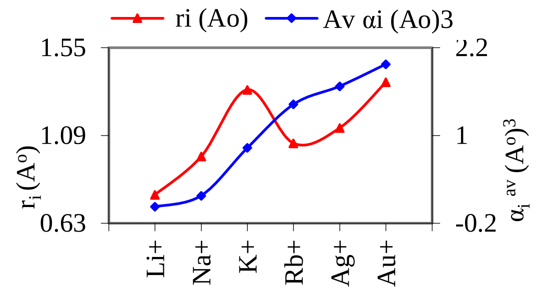

Fig. 3.1 variation of α_i^{av} (A°)^3 & r_i (A°)

Figure 3.1 It shows that the average cation polarizability is increase form 0.0262-1.976 (Ao)^3) and ionic radii also increases from 0.78-1.37(A°). Increasing and decreasing cation polarizability depends upon increasing and decreasing atomic radius.

3.2 Group IIA & IIB: In this group the materials are alkaline earth metals and transition metals. The study is taken on arranging the increasing values of cation electronegativity.

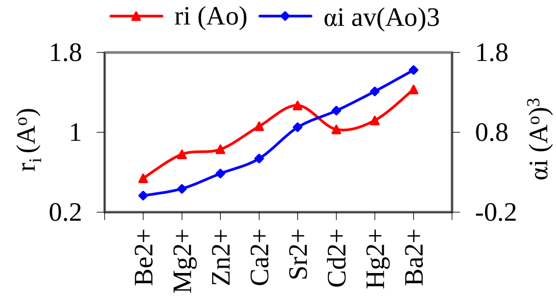

Fig. 3.2 variation of α_i^{av} (A°)^3 & r_i (A°)

Figure 3.2 shows that the average cation polarizability for group IIA and IIB, increase from 0.0075-1.579 (A°)^3) where as for group IIA ionic radii also increases from 0.54-1.43(A°) and for group IIB ionic radii also increases from 1.03-1.12 (A°). Increasing and decreasing cation polarizability depends upon increasing and decreasing atomic radius.

Table 1:

Cation	Outer most Orbital	r_i (A°)	α_i^{av} (A°)^3	Cation	Outer most Orbital	r_i (A°)	α_i^{av} (A°)^3
Li^+	$1s^2$	0.78	0.0265	Be^{2+}	$1s^2$	0.54	0.0075
Na^+	$2p^6$	0.98	0.1780	Mg^{2+}	$2p^6$	0.78	0.0940
K^+	$3p^6$	1.33	0.8310	Ca^{2+}	$3p^6$	1.06	0.4705
Rb^+	$4p^6$	1.049	1.4270	Zn^{2+}	$3d^{10}$	0.83	0.2845
Ag^+	$4d^{10}$	1.13	1.6745	Sr^{2+}	$4p^6$	1.27	0.8630
Au^+	$5d^{10}$	1.37	1.9760	Cd^{2+}	$4d^{10}$	1.03	1.0705
				Ba^{2+}	$5p^6$	1.43	1.5790
				Hg^{2+}	$5d^{10}$	1.12	1.3135

Table 1 shows Cations, Outer most orbital's, Ionic radii r_i(A°) and cation polarizabilities (α_i^{av}(A°)^3.

3.3 Group IIIA & IIIB: The study is taken on arranging the increasing values of cation electronegativity.

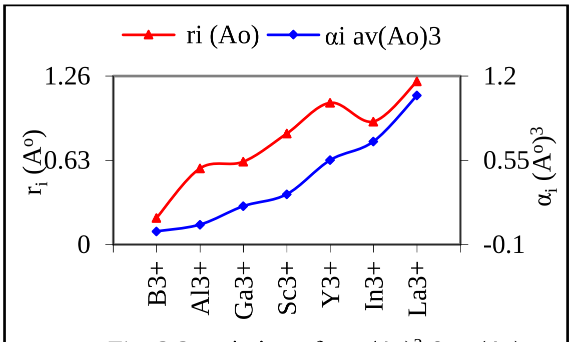

Fig. 3.3 variation of α_i^{av} (A°)^3 & r_i (A°)

Figure 3.3 shows that the average cation polarizability for group IIIA and IIIB, increase from 0.0025-1.05 (A°)^3) where as for group IIIA ionic radii also increases from 0.2-0.92(A°) and for group IIIB ionic radii also increases from 0.83-1.22 (A°). Increasing and decreasing cation polarizability depends upon increasing and decreasing atomic radius.

3.4 Group IVA, IVB: The study is taken on arranging the increasing values of cation electronegativity.

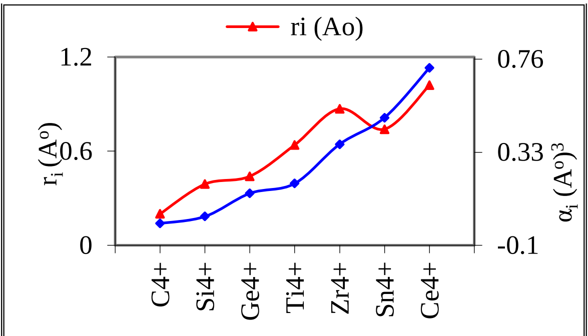

Fig. 3.4 variation of α_i^{av} (A°)^3 & r_i (A°)

Figure 3.4 shows that the average cation polarizability for group IVA and IVB, increase from 0.00115-0.72 (A°)^3) where as for group IVA ionic radii also increases from 0.2-0.74(A°) and for group IVB ionic radii also increases from 0.64-1.02 (A°). Increasing and decreasing cation polarizability depends upon increasing and decreasing atomic radius.

Table 2:

Cation	Outer most Orbital	r_i (A°)	α_i^{av} (A°)^3	Cation	Outer most Orbital	r_i (A°)	α_i^{av} (A°)^3
B^{3+}	$1s^2$	0.20	0.0025	C^{4+}	$1s^2$	0.20	0.00115
Al^{3+}	$2p^6$	0.57	0.0540	Si^{4+}	$2p^6$	0.39	0.03300
Sc^{3+}	$3p^6$	0.83	0.2885	Ti^{4+}	$3p^6$	0.64	0.18550
Ga^{3+}	$3d^{10}$	0.62	0.1965	Ge^{4+}	3d10	0.44	0.14000
Y^{3+}	$4p^6$	1.06	0.5520	Zr^{4+}	$4p^6$	0.87	0.36700
In^{3+}	$4d^{10}$	0.92	0.6960	Sn^{4+}	$4d^{10}$	0.74	0.48950
La^{3+}	$5p^6$	1.22	1.0500	Ce^{4+}	$5p^6$	1.02	0.72000

Table 2 shows Cations, Outer most orbital's, Ionic radii r_i(A°) and cation polarizabilities (α_i^{av}(A°)^3.

Table 3:

Cation	Outer most Orbital	r_i (A°)	α_i^{av} (A°)^3	Cation	Outer most Orbital	r_i (A°)	α_i^{av} (A°)^3
P^{5+}	$2p^6$	0.35	0.021	Mn^{2+}	$3d^5$	0.91	0.544
V^{5+}	$3p^6$	0.59	0.1225	Co^{2+}	$3d^7$	0.82	0.508
As^{5+}	$3d^{10}$	0.4	0.1015	Ni^{2+}	$3d^8$	0.78	0.266
Nb^{5+}	$4p^6$	0.69	0.252	Cu^{2+}	$3d^9$	0.72	0.437
Cr^{6+}	$3p^6$	0.35	0.086	Fe^{3+}	$3d^5$	0.67	0.437
Se^{6+}	$3d^{10}$	0.35	0.074	Sb^{3+}	$5s^2$	0.9	1.111
Mo^{6+}	$4p^6$	0.65	0.1795	Bi^{3+}	$6s^2$	1.2	1.508
				Te^{4+}	$4d^{10}$	0.89	1.595

Table 3 shows Cations, Outer most orbital's, Ionic radii r_i(A°) and cation polarizabilities (α_i^{av}(A°)^3.

3.5 Group VA, VB, & Group VIA, VIB: Here these two groups are plotted due to less number of cations. The study is also taken on arranging the increasing values of cation electronegativity

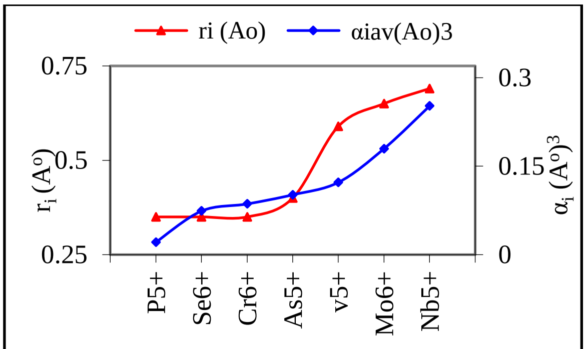

Fig. 3.5 variation of α_i^{av} (A°)^3 & r_i (A°)

Figure 3.5 shows that the average cation polarizability for group VA, VB, and VIA, VIB increase from 0.021- 0.252 (A°)^3) where as for group VIA ionic radii also increases from

0.35- 0.69(A°) and for group VIB ionic radii also increases from 0.35-0.65 (A°). Increasing and decreasing cation polarizability depends upon increasing and decreasing atomic radius.

3.6 Other group: The values of cation polarizability from other sources with their ionic radii are as follows,

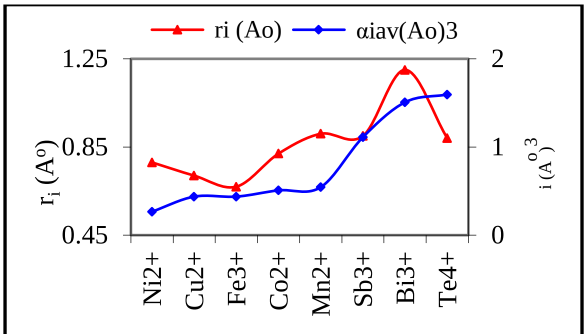

Fig. 3.6 variation of α_i^{av} $(A^o)^3$ & r_i (A°)

Figure 3.6 shows that the average cation polarizability from other sources for random groups increase from 0.266 – 1.595 $((A^o)^3)$ where as ionic radii also increases for 2^+ from 0.72-0.91(A°) and for 3^+ ionic radii also increases from 0.67 – 1.2 (A°) and for 4^+ it is 0.89. Increasing and decreasing cation polarizability depends upon increasing and decreasing atomic radius.

CONCLUSION

From the review of ionic radii and cation polarizability it clears that in all cations, cation polarizability decreases, ionic radii also decreases but in case of cations from other sources ionic radii increase also increases cation polarizability. Polarizing power of the cation is directly proportional to the charge on a cation and inversely proportional to the size of the cation. In other words, greater the charge, higher the polarizing power. Smaller the cation, higher the polarizing power. The electronegativity increases with the positive oxidation state of the atom, as the tendency to attract an electron will increase with the positive charge of the cation. As an s electron is nearer the nucleus due to its penetrating power, the electronegativity increases with the increasing s character of the hybrid orbital's. The electronegativity increases with the (partial) positive charge on the atom. Increasing and decreasing cation polarizability depends upon increasing and decreasing atomic radius. Descending order of average cation polarizabilities are of Pb^{2+}, Te^{4+}, Ba^{2+}, Hg^{2+} and La^{3+} cations, irrespective of atomic radius due to these cations are not in same group but they from same sixth period except Te^{4+}.

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