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Near-equivalence of the role of structural unpinning number, basicity and reciprocal average electronegativity in determining the conductivity of glasses

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ABSTRACT

The chemical approach made to investigate the origin of fast ion conduction in AgI-based fast ion conducting (FIC) glasses has been extended to various ionically conducting systems containing Na^+ ion. An index known as structural unpinning number (SUN), S, has been defined for this purpose based on the unscreened nuclear charge on the cation and the average electronegativity of all the anions. Variation of the log(conductivity), at a given temperature, as a function of structural unpinning number, optical basicity, λ , and the reciprocal average electronegativity of all the anions, $1/\chi_a$, has been examined for a number of Na^+-ion conducting glasses and a nearly identical variation has been noticed in all the cases. The equivalence of these chemical parameters as determinants of the conductivity behavior of glasses has thus been established and the origin of this equivalence has been discussed.

INTRODUCTION

Fast ion conducting glasses generally consist of anions of low electronegativity and cations of high unscreened nuclear charge [1]. This causes a redistribution of electronic charges resulting from a reverse charge transfer from anions to cations due to anion-cation interaction [2]. The actual charge on the conducting cation can, therefore, be expected to be lower than its formal charge. The reduction of the electrical charge on cation results in the decrease in the depth of the potential well which becomes relatively shallow [3]. These features together make it appear that cations are 'pulled- up' from otherwise deep potential wells. This is the essence of structural unpinning model.

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Structural unpinning is quantified using a dimensionless 'structural unpinning number', S, which is given by

$$S = C\,[Z^*/\chi_a]\,[V_m/N] \qquad (1)$$

Where, Z^* is the effective nuclear charge on the cation (calculated using Slater's rules [4]), χ_a is the average electronegativity of all the anions (obtained employing Sanderson's method [5]), V_m/N is the effective volume available for the cation for its motion in a mole of the glass and C is a constant which renders S non-dimensional.

A plot of isothermal logσ vs S for a variety of glasses has been found [1] to give rise to a smooth variation which could be described using a simple relation

$$\ln\sigma = \ln\sigma_l/(1-e^{-aS}) \qquad (2)$$

Where, σ_l is the limiting isothermal conductivity at high values of S and 'a' is a numerical constant dependent on the cation.

Hunter and Ingram [6] have recognised a rather similar variation when logσ is plotted as a function of (calculated) optical basicity, λ. This observation suggests a possible relation between S and λ.

DISCUSSION

In order to investigate the underlying relation between S and λ, we have calculated S, using equation (1), for borate, silicate and aluminoborate glasses of sodium for which the variation of logσ has been studied as a function of λ [6]. Plots of logσ vs λ and logσ vs S are shown in figs. 1 and 2, respectively. The similarity is rather striking.

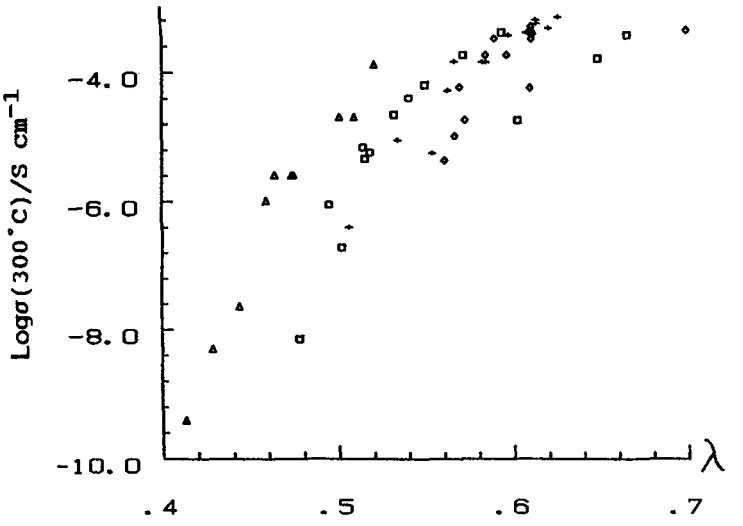

Fig. 1. Variation of the conductivity (at 300°C) with the calculated optical basicity, λ.
+ = Na_2O-SiO_2 Δ = Na_2O-B_2O_3 o = Na_2O-B_2O_3-SiO_2
□ = Na_2O-Al_2O_3-B_2O_3 ◊ = Na_2O-Al_2O_3-SiO_2

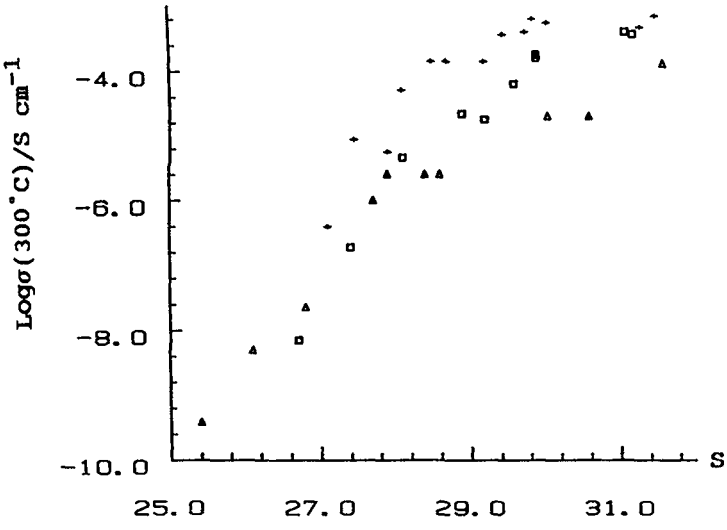

Fig. 2. Variation of the conductivity (at 300°C) with the structural unpinning number, S (symbols, as given in fig. 1).

The optical basicities used by Hunter and Ingram have been based on the red-shifts observed in the UV absorption edges of probe cations Tl^{+}, Pb^{2+} or Bi^{3+} [7,8]. Hence the basicities essentially represent the effect of anion matrices on the probe cations in terms of their electron (or oxide ion) donating abilities. Since electron donating ability is inversely related to electronegativity (χ), $1/\chi$ is also a measure of the basicity. For the same cation, therefore, plot of logσ vs λ is equivalent to a plot of logσ vs $1/\chi_a$. Fig. 3 gives logσ vs $1/\chi_a$ for comparison. The variation in figs. 1, 2 and 3 is strikingly similar.

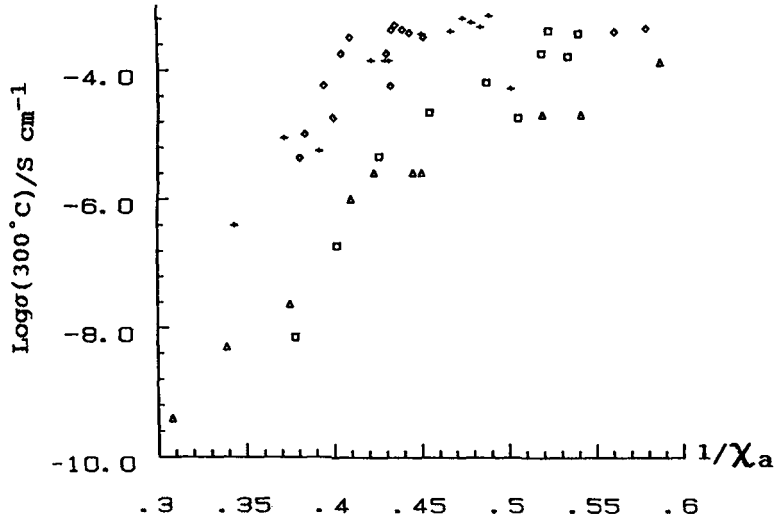

Fig. 3. Variation of the conductivity (at 300°C) with the reciprocal average electronegativity of all the anions, $1/\chi_a$ (symbols, as given in fig. 1).

Evidently, the relation between basicity and structural unpinning number is uniquely determined through the average electronegativity of the anions for any given cation like Na^+, Ag^+ or Li^+. Hence the plots of logσ vs $1/\chi_a$ or S would be equivalent, since the variation of V_m/N is itself small by comparison. By choosing a suitable scale the near-equivalence of these plots can be demonstrated [9].

CONCLUSIONS

The near-equivalence of S, Λ and $1/\chi_a$ in determining the conductivity of the glass, has been demonstrated employing a variety of Na^+-ion conducting glasses. The complete equivalence of S and optical basicity for glasses with the same conducting cation is, however, dependent on similarity in V_m/N values for a series of such glasses. The usefulness of such universal plots would be enhanced if the basicity of the glasses could be estimated reliably without requiring optical data, such as by the use of $1/\chi_a$.

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