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Glass formation and high conductivity in the
ternary system silver iodide + silver arsenate
(Ag_3AsO_4) + silver metaphosphate (AgPO_3):
host to glassy .alpha.-silver iodide?

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that the inverse viscosity dependence of k_{nr} found earlier for DHICC in primary alcohols persists in the micelle environment. If this assumption was wrong, the value of 4.3 cP would be likely to be an underestimate.

If the most plausible explanation for the reduced value of the nonradiative rate activation energy for the micelle-attached dye is that the torsional barrier crossing is influenced by the nonisotropic Brownian motion of surfactant monomers at the micelle surface, it may be possible to gain further insight into this question by performing measurements with related dyes. The dye 1,1'-diocetadecyl-3,3',3'-tetramethylindocarbocyanine iodide, which has the same chromophore, would be expected to have a similar value of E^0 . It would be of interest to measure the EMV felt by this dye, together with the apparent activation energy for the nonradiative rate. Such a dye might be less influenced by effects associated with the micelle surface.

Conclusions

The major component of the nonradiative rate in DHICC has been found to have an inverse dependence on the medium viscosity. This is compatible with excited-state barrier crossing describable by the Smoluchowski limit of Kramers' equation. The sensitivity of the nonradiative rate of DHICC to restriction of excited-state torsion, in principle, provides a sensitive measure of effective microviscosity in micelles. The value of EMV for SDS micelles

assessed in this way lies at the lower end of the range of values determined by other methods.¹²⁻¹⁴ This is compatible with the dye probing the surface region of the micelle. Our value of 4.3 cP is comparable to the value of ca. 2 cP found recently by measurement of the nonradiative rate in the related dye, pinacyanol iodide.⁴² Absolute values of EMV determined in this way are equivocal to the degree that they are based on the assumption that the viscosity dependence of $k_{nr}(\eta)$ determined in homogeneous solution holds for the micelle-attached dye. The low value for the apparent activation energy for k_{nr} for the micelle-attached DHICC also suggests that the coupling between the excited-state torsional motion and Brownian motion within the micelle may differ from that in homogeneous solution. Notwithstanding these doubts concerning the absolute value of the EMV, it is clear that quantum yield measurements on DHICC can provide a sensitive probe of changes in the EMV associated with changes in the micelle surface.

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Registry No. PHICC, 95646-75-6; SDS, 151-21-3; urea, 57-13-6.

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Glass Formation and High Conductivity in the Ternary System $\text{AgI} + \text{Ag}_3\text{AsO}_4 + \text{AgPO}_3$: Host to Glassy AgI?

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Wide regions of glass formation have been found in the ternary system $x\text{AgI} + y\text{Ag}_3\text{AsO}_4 + (1-x-y)\text{AgPO}_3$. Glasses containing up to 75 mol % AgI can be formed in sections greater than 2 cm thick without signs of devitrification. Glass transition temperatures as high as 175 °C for glasses containing ~10 mol % AgI fall to ~45 °C at the highest AgI content. An equivalent ratio of $\text{AgI}:N$ is defined and it is found that, for all glass-forming compositions, the electrical data as expressed in the Arrhenius form, $\sigma = A \exp(-E_{act}/RT)$, $\log(\sigma/(\Omega \text{ cm})^{-1})$, $\log(A/(\Omega \text{ cm})^{-1})$, $E_{act}/(\text{kcal mol}^{-1})$, and additionally T_g/K , can be described as linear functions of N . These data are used to give support to the view of these glasses as being hosts to a "liquidlike" AgI giving rise to the high conductivity they exhibit, as high as $0.0143 (\Omega \text{ cm})^{-1}$ at room temperature for glasses containing the maximum AgI. Finally, from these linear relationships, functions for the mobility μ and number of the mobile Ag^+ cations n are developed.

Introduction

Many high ionic conductivity glasses have been recognized and studied in the recent past. Some of these have been prepared by adding AgI to a mixture of a glass forming Lewis acid, e.g., P_2O_5 ,¹⁻⁴ or B_2O_3 ,^{5,6} and Ag_2O , acting as modifier: and in many cases high

ionic conductivity glasses can be found within a pseudobinary $\text{AgI}-\text{Ag}$ oxysalt,⁷ the corresponding glass formation region being restricted along a single line⁸ of the ternary phase diagram $\text{AgI}-\text{Ag}_2\text{O}-\text{Lewis acid}$. This is the case of the glasses prepared from $\text{AgI}-\text{Ag}_2\text{MoO}_4$, $\text{AgI}-\text{Ag}_2\text{CrO}_4$, $\text{AgI}-\text{Ag}_3\text{AsO}_4$, etc.; a simple explanation of this limitation might be found in the poor glass-forming character of the Lewis acid concerned, which, at normal pressure, is generally not able to form a stable glass either by itself or with added Ag_2O .

One then should attribute to AgI some peculiar modifying property enabling the formation and stabilization of glasses such as $4\text{AgI}:\text{Ag}_3\text{AsO}_4$ ⁹⁻¹² and $3\text{AgI}:\text{Ag}_2\text{MoO}_4$.¹³ It should be noticed

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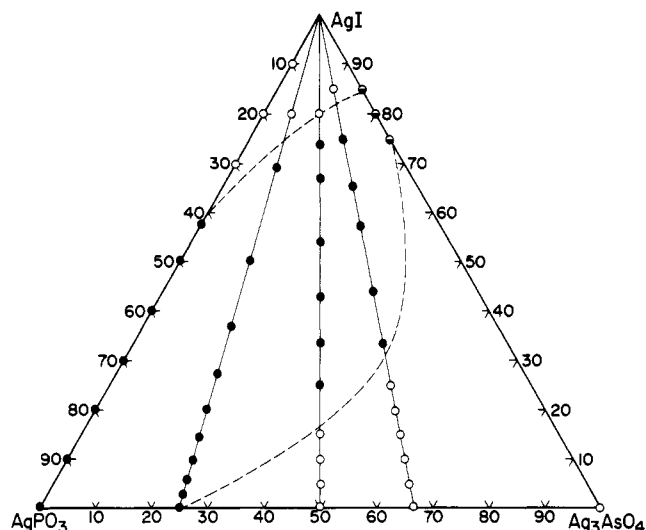


Figure 1. Glass-forming region in ternary system AgI + Ag₃AsO₄ + AgPO₃. Filled circles are glass-forming, half-filled circles are glass-forming only in thin sections, and open circles are devitrified.

AgI is present in both these glasses with an equivalent fraction of about 0.6 and that this value corresponds to the extreme limit of the glass formation region of every AgI based high conductivity glassy system studied so far, (see ref. 7 and below), independent of the width of the corresponding glass formation region. This composition also corresponds to the highest conductivity at room temperature, which is more or less, the same for all such glasses, viz. $2\text{--}4 \times 10^{-2} (\Omega \text{ cm})^{-1}$.⁷

Accordingly, it seems that, whenever the glassy state is formed and stabilized, the role of AgI is to act as a source of mobile ions responsible for the high conductivity. In an effort to explore this role of AgI more fully, AgI has been added to mixtures of AgPO₃ and Ag₃AsO₄, the former of which can easily give glass by itself,^{3,14} whereas the latter is stable only as a crystal modification. The corresponding ternary system has been investigated along the pseudobinary lines AgI + (*n*AgPO₃:*m*Ag₃AsO₄), with *n*:*m* ratios of 1:2, 1:1, and 3:1. The results describing the binaries AgI + AgPO₃ and AgI + Ag₃AsO₄ correspond to those of previous investigations by other authors.^{3,9,10}

The binary system AgI + Ag₃AsO₄ has been found⁹⁻¹² to yield glasses only for liquid nitrogen quenched droplets from the hot melt in a very small region about 80 mol % AgI. Indeed, room temperature quenches of these compositions in our laboratory gave glasses only in the thinnest (<0.5 mm) sheets. On the other hand, the system AgI + AgPO₃, for AgI mole fractions less than 50 mol %, yields glasses in large sections, though ionic conductivity falls off sharply.^{2,4,15}

Experimental Section

Preparation of the Glasses. Charges of AgI, AgNO₃, (N-H₄)H₂PO₄, and Ag₃AsO₄ were prepared to yield compositions along tie lines of the ternary diagram AgI + Ag₃AsO₄ + AgPO₃ (see Figure 1). AgI was prepared by precipitation of AgNO₃ with NaI followed by careful drying and powdering of the precipitate. Ag₃AsO₄ was prepared by precipitation of AgNO₃ with Na₂HAsO₄·2H₂O, again followed by careful drying and powdering of the precipitate. (NH₄)H₂PO₄ and AgNO₃ were of reagent

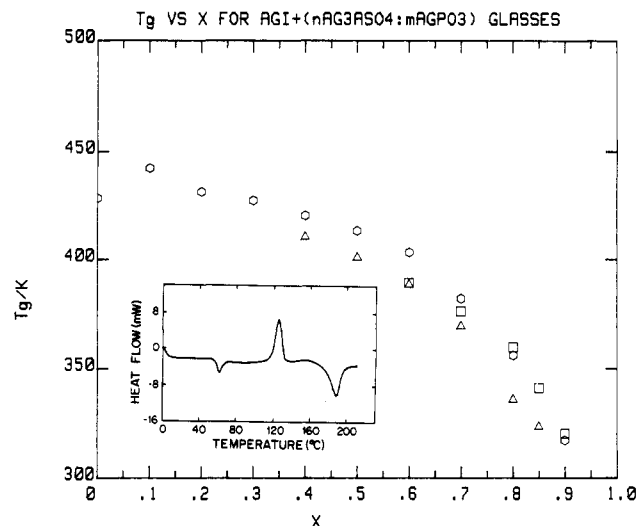


Figure 2. Glass transition temperatures for three series of glasses belonging to the ternary system: squares for the series *x*AgI + (1 - *x*)(2Ag₃AsO₄:AgPO₃), triangles for *x*AgI + (1 - *x*)(Ag₃AsO₄:AgPO₃), hexagons for *x*AgI + (1 - *x*)(Ag₃AsO₄:3AgPO₃). A typical DSC scan for a 0.85 AgI + 0.15(Ag₃AsO₄:AgPO₃) glass at the heating rate of 10 °C/min is shown in the insert. *T_g* is defined as onset of the endothermic transition.

grade and were used without further purification.

To fully examine the ternary system, fixed ratios (Ag₃AsO₄:AgPO₃) were chosen of 2:1, 1:1, and 1:3. AgPO₃ was prepared in situ from appropriate amounts of AgNO₃ and (NH₄)H₂PO₄, assuming complete delivery of NO₂, H₂O, and NH₃ from the melt.¹⁶ Fusion was carried out in open porcelain crucibles for a period of ~15 min after cessation of gas evolution. Careful fusion techniques were used to ensure against compositional changes due to sputtering of the charge during fusion. Weight loss measurements on all samples showed a maximum weight change of ~0.50 wt %, with the average being about 0.20 wt %, beyond that calculated for complete loss.

DSC Measurements. Samples from the quenching block, typically 50–100 mg, were encapsulated in silver sample pans and scanned in the temperature range from 0 to 10–50 °C above *T_g* at 10 °C/min, using a Dupont 1090 DSC. Marginal glass-forming samples showed exothermic transitions only a few degrees above *T_g*, whereas other compositions showed no transitions above *T_g*. A typical DSC scan is shown in Figure 2, insert.

Electrical Measurements. Glassy disks were quenched from the melt into stainless steel molds at room temperature yielding samples 10 mm × 1–2 mm. Gold electrodes were sputtered onto the samples by using a Technics Hummerll equipped with a water-cooled stage to guard against thermal treatments leading to crystallization, especially for low *T_g* glasses, during electrode sputtering. Exact cell constants were determined by polishing the sample faces and using a micrometer (±0.03 mm). The electrode diameter was fixed through a machined mask.

Ionic conductivities were measured over the temperature range –160 to 65 °C with a Wayne-Kerr B331 autobalance impedance bridge at fixed frequency of 1592 Hz. Frequency scans on similar samples⁹ showed that for temperatures of –100 °C and above this frequency lies well on the “plateau” region of the frequency dependence of the conductivity.⁴ This frequency independent plateau has been carefully identified with the true value of the dc conductivity.¹⁷ For temperatures below –100 °C, systematic deviation to higher conductivities were found indicating the presence of relaxation contributions to the conductivity.⁹

The temperature dependence of the dc conductivity over this range of temperatures is reported in the Arrhenius form

$$\sigma = Ae^{-E_{act}/RT} \quad (1)$$

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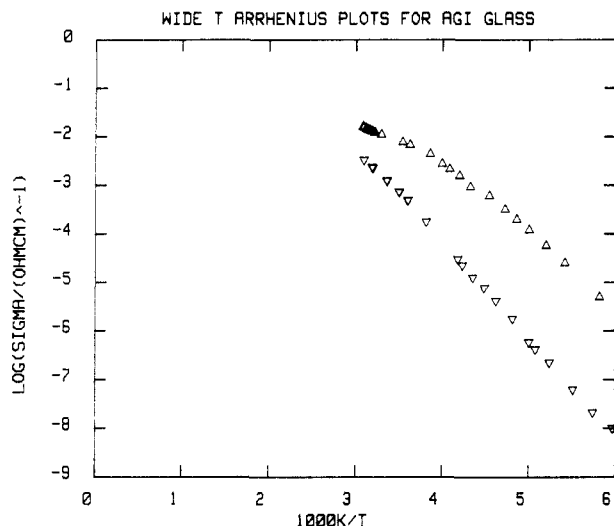


Figure 3. Arrhenius plots over wide temperature range -100 to 65 °C for 0.85 AgI + $0.15(\text{Ag}_3\text{AsO}_4:\text{AgPO}_3)$ and $0.70\text{AgI} + 0.30(\text{Ag}_3\text{AsO}_4:\text{AgPO}_3)$ glasses showing a distribution of activation energies as evidence from the curvature. The "knee" in the Arrhenius plot does not correspond to a thermal effect in DSC over the same temperature range.

where the symbols have their usual meanings.¹⁸

No significant change either of σ or of its T dependence was observed after 1 year storage of the samples.

Results

Glass Formation Region. In Figure 1 the glass-forming region (for room temperature quenches) for the ternary system $x\text{AgI} + y\text{Ag}_3\text{AsO}_4 + (1-x-y)\text{AgPO}_3$ is given. Filled circles denote strong glass-forming compositions, half-filled circles marginal glass formation, and open circles devitrified melts on cooling. Limits for the binary systems $\text{AgI} + \text{AgPO}_3$ ⁴ and $\text{AgI} + \text{Ag}_3\text{AsO}_4$ ⁹ are also given.

Glass Transition Temperatures. In Figure 2, T_g 's are given for the three "pseudo-binary" series: $\text{AgI} + (2\text{Ag}_3\text{AsO}_4:\text{AgPO}_3)$, $\text{AgI} + (\text{Ag}_3\text{AsO}_4:\text{AgPO}_3)$, and $\text{AgI} + (\text{Ag}_3\text{AsO}_4:3\text{AgPO}_3)$. All T_g 's tend to ~ 170 °C for $x\text{AgI}$ small (here x refers to the pseudobinary mole fraction), but with increasing x , T_g decreases and then drops to a low value for the highest x (see below). In view of the recent structural data⁷ indicating that AgI does little to the structural units of the oxide glass but rather tends to "open up" the structure through the incorporation of iodide polyhedra, this viscosity lowering effect is possibly the cause for decreasing T_g with increasing x . The accelerating nature of this decrease for large x could be due to a critical composition of AgI above which the structure strengthening oxysalt network decays rapidly.

Electrical Measurements. In Figure 3, Arrhenius plots of the conductivity for two glasses in the system $\text{AgI} + [\text{Ag}_3\text{AsO}_4:\text{AgPO}_3]$ are given for the full temperature range covered in this study. At ~ 50 °C, the Arrhenius plots for glasses of highest AgI content exhibit a change in slope to pass to a higher-temperature low-activation energy region. This "knee" effect is evidently related to the fraction of AgI in the glass, as samples containing fractions of AgI less than 70 mol % AgI show almost no effect. Low-temperature DSC measurements on glasses showing a "knee" in the Arrhenius plots in this temperature range to give no indication of a thermal transition, though a broadened second-order transition is not ruled out. Within the error limits of our data, a curvature in the data, representative of liquidlike behavior, may well be the case here. Indeed, careful measurements by Ingram et al.¹⁹ on the binary glass $\text{Ag}_7\text{I}_4\text{AsO}_4$ have shown that non-Arrhenius behavior of this kind occurs; it has been attributed to a "liquidlike

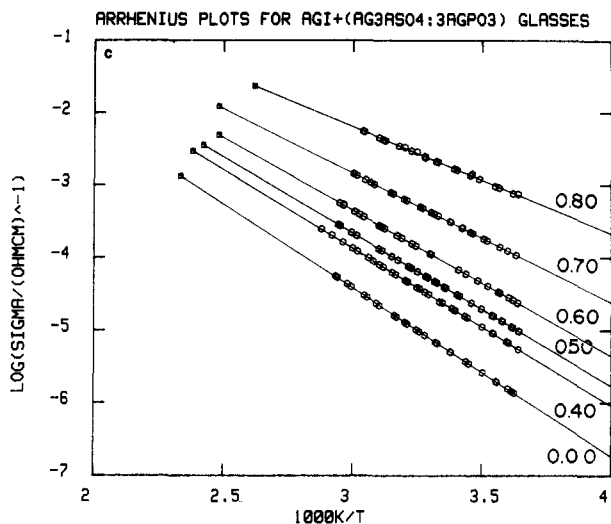
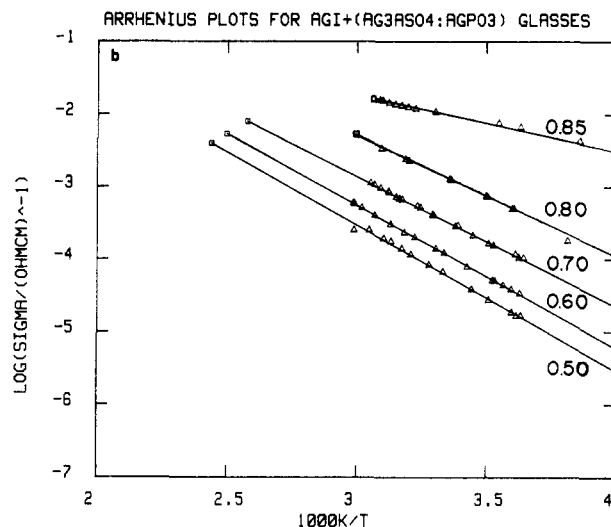
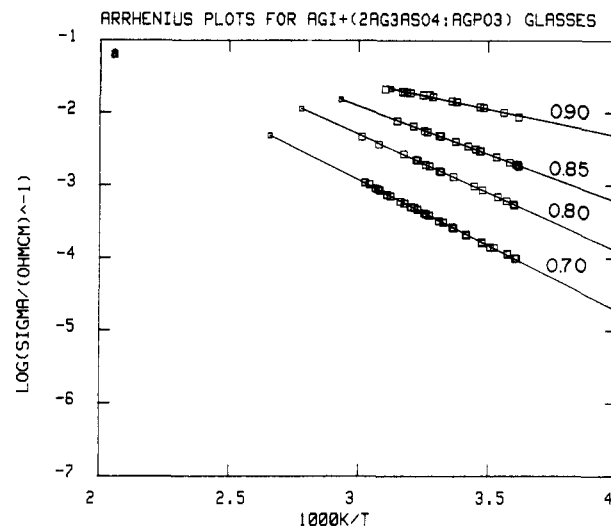


Figure 4. (a) Arrhenius plots of the ionic conductivity for glass series $x\text{AgI} + (1-x)(2\text{Ag}_3\text{AsO}_4:\text{AgPO}_3)$. Temperature range accords to the high temperature low-activation energy region. (b) Arrhenius plots for glass series $x\text{AgI} + (1-x)(\text{Ag}_3\text{AsO}_4:\text{AgI})$. (c) Arrhenius plots for glass series $x\text{AgI} + (1-x)(\text{Ag}_3\text{AsO}_4:3\text{AgPO}_3)$.

motion of the anions I^- and AsO_4^{3-} , rather than of the mobile cations Ag^+ . The possibility of a "liquidlike" sublattice of the mobile cations Ag^+ giving rise to the curvature in the Arrhenius plots will be discussed below. More extensive experiments are planned to further investigate this behavior in these glasses.

In Figures 4–6 Arrhenius plots for the glasses $x\text{AgI} + (1-x)[2\text{Ag}_3\text{AsO}_4:\text{AgPO}_3]$, $x\text{AgI} + (1-x)[\text{Ag}_3\text{AsO}_4:\text{AgPO}_3]$, and

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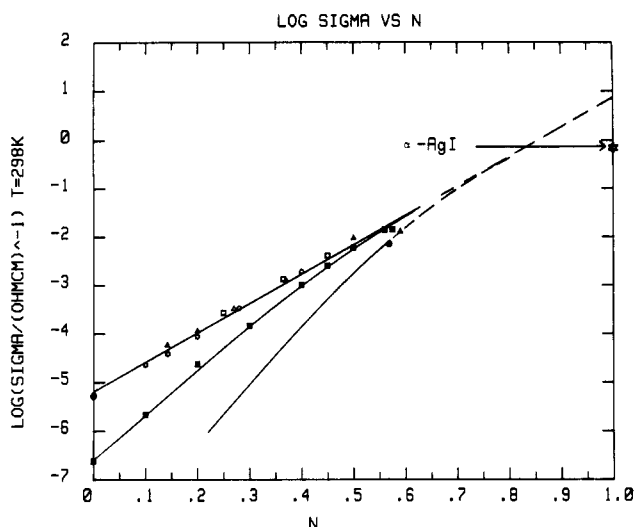


Figure 5. Composition dependence of the room temperature conductivity for ternary glasses: open squares, AgI + (2Ag₃AsO₄:AgPO₃); open triangles, AgI + (Ag₃AsO₄:AgPO₃); open hexagons, AgI + (Ag₃AsO₄:3AgPO₃), using equivalent fraction N as composition variable. Binary glass data (filled squares, AgI + AgPO₃; filled circles, AgI + Ag₃AsO₄) are included, from ref 2 and 9, respectively.

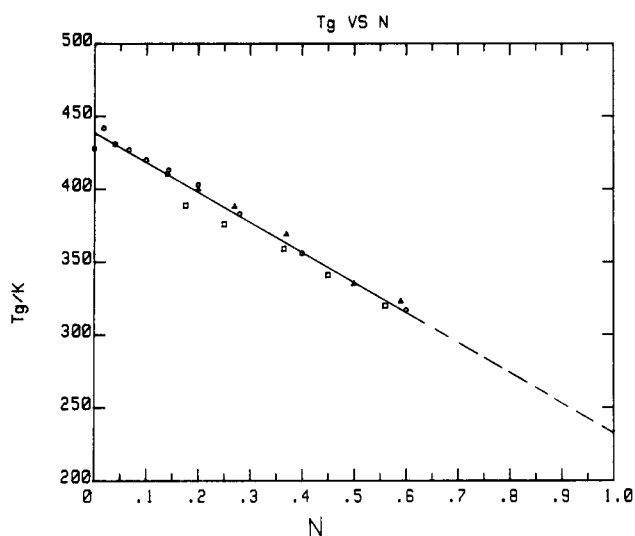


Figure 6. Equivalent fraction dependence of T_g in ternary silver glasses. Symbols as in Figure 5.

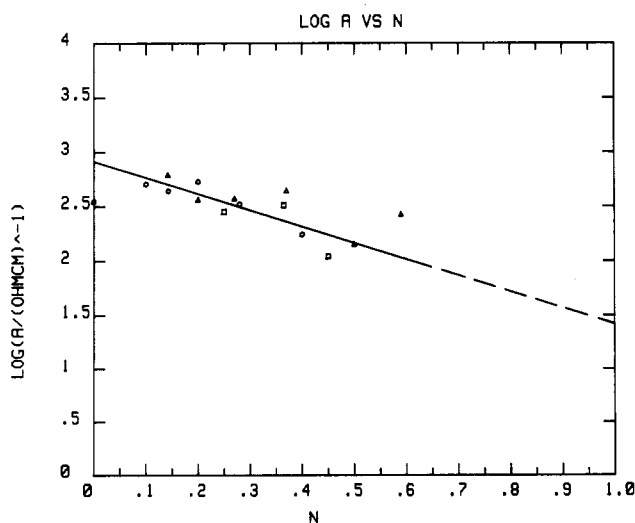


Figure 7. Equivalent fraction dependence of the preexponential factor A for ternary silver glasses. Symbols as in Figure 6. Preexponential factors are taken from least-squares fitted Arrhenius plots.

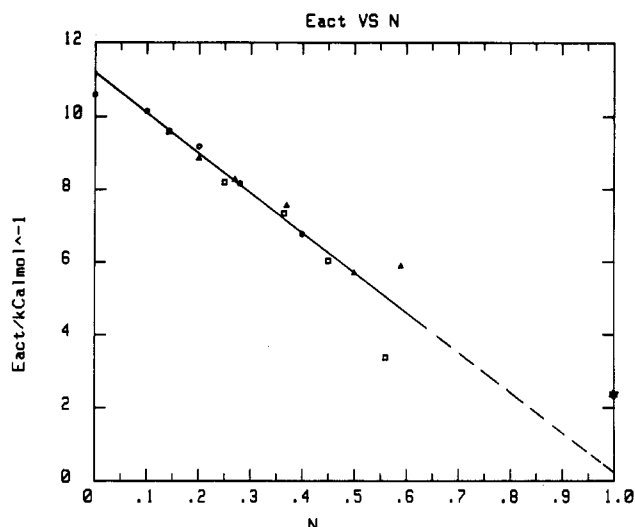


Figure 8. Equivalent fraction dependence of E_{act} for ternary silver glasses. Extrapolation to $N = 1$, for glassy AgI, shows vanishing activation energy of 0.240 kcal mol⁻¹. The value for α -AgI is included for comparison.

TABLE I

$x(\text{AgI})$	$x'(\text{AgI})$	$N(\text{Ag}^+)$	$T_g/^\circ\text{C}$	$\log(\sigma_{25}/(\Omega\text{ cm})^{-1})$	$E_{act}/(\text{kcal mol}^{-1})$	$\log(A/(\Omega\text{ cm})^{-1})$
AgI + 2Ag ₃ AsO ₄ :AgPO ₃						
0.90	0.75	0.563	47	-1.85	3.38	0.63
0.85	0.65	0.447	68	-2.378	6.03	2.04
0.80	0.57	0.364	87	-2.867	7.34	2.51
0.70	0.44	0.250	103	-3.562	8.21	2.45
0.60	0.33	0.176	116			
AgI + Ag ₃ AsO ₄ :AgPO ₃						
0.85	0.74	0.586	50	-1.92	3.42	0.58
0.80	0.67	0.500	63	-2.02	5.69	2.15
0.70	0.54	0.368	96	-2.89	7.55	2.64
0.60	0.43	0.273	115	-3.49	8.27	2.57
0.50	0.33	0.200	128	-3.94	8.87	2.56
0.40	0.25	0.143	137	-4.23	9.58	2.79
AgI + Ag ₃ AsO ₄ :3AgPO ₃						
0.90	0.69	0.600	44			
0.80	0.59	0.486	83	-2.72	6.77	2.24
0.70	0.50	0.400	110	-3.47	8.17	2.52
0.60	0.37	0.280	130	-4.06	9.20	2.69
0.50	0.20	0.143	140	-4.41	9.62	2.64
0.40	0.14	0.100	147	-4.64	10.02	2.71
0.30	0.097	0.066	155			
0.20	0.059	0.040	158			
0.10	0.027	0.018	169			
0.00	0.00	0.00	155	-5.24	10.60	3.52

$x\text{AgI} + (1-x)[\text{Ag}_3\text{AsO}_4:3\text{AgPO}_3]$, respectively, are given for the higher-temperature low-activation energy region about room temperature. Lines drawn through the data are linear least-squares fits. The electrical properties, E_{act} (activation energy), $\log(\sigma_{298}/(\Omega\text{ cm})^{-1})$, and $\log(A/(\Omega\text{ cm})^{-1})$, obtained from these fits, are tabulated along with the DSC and composition data in Table I.

Discussion

Using the conductivity and T_g data, we develop three major points in this section. First, we address the possibility of a "mixed anion" effect, as introduced by Magistris et al.,²⁰ in these ternary glasses and its dependence upon the composition variable chosen for study. Secondly, using the dependence of the conductivity upon mobility μ , and number of available charge carriers n , $\sigma = n\mu e$,^{21,22} we develop an empirical relationship for the conductivity in terms of the equivalent fraction of Ag cations N (to be defined below).

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Finally, based on this relationship between conductivity and N , we postulate a new phase of AgI, a liquidlike phase, thought to be stabilized to low temperatures by the oxyanion glass-forming framework.

Mixed Anion Effect in Glass. The extrapolation of the composition dependence of the room temperature conductivity in similar AgI + Ag oxyanion glasses to that of α -AgI has been shown by other workers⁷ to occur linearly when using the total mole fraction AgI as the composition variable, i.e.

$$x(\text{AgI}) = \frac{[\text{AgI}]}{[\text{AgI}] + [\text{AgPO}_3]} \quad (2)$$

for data reported in ref 7. We briefly examine this behavior qualitatively here and in more quantitative detail below with the present extensive data set. If the extrapolation to α -AgI ($x\text{AgI} = 1$) is valid, then the compositional variable must be chosen carefully. To consider that the glass imitates α -AgI at low temperatures (below the α - β transition) then that fraction of Ag^+ in the glass arising from the AgI content (an equivalent fraction of Ag^+) would appear as a more appropriate compositional variable. This approach treats the base glass as a poor conductor and views only those Ag cations coming from AgI dissociation as the mobile charge carriers (see below). If this is indeed the case, then the ionic conductivity in the ternary glasses may coalesce to a single function in the composition plot when using this equivalent fraction, i.e., the phosphate-arsenate oxyanion network is thought to have little influence on the "migration pathways" of Ag^+ in these glasses across the ternary diagram.

That this is the case is indicated in Figure 5. Here we have calculated the fraction of Ag^+ arising from AgI (the equivalent fraction) as

$$N_{\text{Ag}^+}(\text{AgI}) \equiv N = \frac{[\text{AgI}]}{[\text{AgI}] + [\text{AgPO}_3] + 3[\text{Ag}_3\text{AsO}_4]} \quad (3)$$

and we note that for a binary such as AgI + AgPO₃, N is equal to the total fraction AgI. Using least-squares linear regression on the data of Figure 5, we find that the intercept $\log(\sigma_{298}(\Omega \text{ cm})^{-1}) = +0.855$ for $N_{\text{Ag}^+}(\text{AgI}) = 1$ is much larger than that of $\log(\sigma_{298}(\Omega \text{ cm})^{-1}) = 0.100$ predicted from extrapolation of Arrhenius data below the $\alpha \rightarrow \beta$ transition to room temperature for α -AgI.¹

Microscopically, we may assume that this series of data lend support to the view that some type (see below) of extended AgI phase is stabilized to low temperatures by the base oxide glass network. As these glasses are fully transparent, these structures must indeed be microscopic and homogeneous, though a microscopically heterogeneously phase-separated system seems to be excluded here.

Additionally, in Figure 5 a new feature, introduced above, is evident. When the ternary system data are compared to the binary data, i.e., AgI + Ag₃AsO₄, AgI + AgPO₃, the ternary glasses show an enhanced conductivity over the binary glasses for the same equivalent fraction of AgI. This behavior tends to support a "positive" mixed anion effect upon the transport properties in these ternary glasses that has been suggested earlier by Magistris et al.²⁰ concerning glasses of the AgI + Ag₂O + (B₂O₃:P₂O₅) type. Here this effect may support the observation that the properties of these Ag electrolytes can be significantly enhanced by using mixed anion type base glasses as they may show enhanced properties, viz., a higher ionic conductivity, at the same fraction of AgI doping.

Relationship of Ionic Conductivity and T_g to Equivalent Fraction of AgI (N). To gain a better insight into the compositional dependencies of the measured electrical and thermal properties, the equivalent fraction of AgI, N , has been chosen (as introduced above) to quantitatively fit every property evaluated in the present work. N may be expressed in terms of the AgI molar fraction of each pseudobinary AgI + ($n\text{Ag}_3\text{AsO}_4:m\text{AgPO}_3$) as follows:

$$N = \frac{x}{x + (1-x)(3n+m)} \quad (4)$$

or

$$N = \frac{X_I}{X_I + 3X_{\text{As}} + X_{\text{P}}} \quad (\text{with } X_I + X_{\text{As}} + X_{\text{P}} = 1) \quad (5)$$

where I, As, and P refer to AgI, Ag₃AsO₄, and AgPO₃, respectively.

The whole body of the experimental results may be then be reproduced with the following least-squares fitted linear equations:

$$E_{\text{act}}/(\text{kcal mol}^{-1}) = 11.20 - 10.96N \equiv a - bN \quad (6)$$

$$\log[A/(\Omega \text{ cm})^{-1}] = 6.724 - 3.446N \equiv c - dN \quad (7)$$

$$\log[\sigma_{298}/(\Omega \text{ cm})^{-1}] = -5.168 + 6.023N \quad (8)$$

$$T_g/\text{K} = 438.15 - 205.04N \quad (9)$$

where N is calculated for each pseudobinary glass as above, and σ_{298} is defined as the dc conductivity at $T = 298 \text{ K}$.

Substituting the expressions for $E_{\text{act}}/(\text{kcal mol}^{-1})$ and $A/(\Omega \text{ cm})^{-1}$, eq 6 and 7, respectively, into the Arrhenius eq 1 yields

$$\sigma(N, T) = \exp(c - dN) \exp[-(a - bN)/RT] \quad (10)$$

$$\equiv \sigma_0(T)[F(T)]^N \quad (11)$$

where

$$\sigma_0(T) \equiv \sigma_{N=0}(T) = \exp(c - a/RT) \quad (12)$$

and

$$F(T) \equiv \exp(b/RT - d) \quad (13)$$

Since $\sigma_0(T)$ does not depend on N , it may be phenomenologically considered as a character of the oxide glass matrix hosting AgI. If we assume that $(\sigma/\sigma_0)^{1/N}$ is proportional to the probability of charge migration due to a single ion, then

$$\sigma/\sigma_0 = [F(T)]^N \propto P \quad (14)$$

where here P would give the total probability dealing with the whole population of the mobile ions per unit volume, each one of which is thought of as an independent carrier for charge migration. Hence, the process of charge transport would be described in terms of simultaneous and mutually independent single ion contributions. Addition of AgI to the base glass then would increase the number of such single ion contributions to σ and decreases the phenomenological activation energy, E_{act} . Finally, due to the fact that d is less than b/RT for all $T < T_g$, P would decrease with increasing T , for all N . This may arise from a decorrelation effect of the thermal activation of the random walk drifts, i.e., from strong interaction between thermalized phonon modes of the base glass framework and ionic conduction modes. For $N = 1$ (all AgI), $P = P_{\text{max}}$ and, as $a \sim b$, eq 10 shows that σ becomes almost independent of T viz., vanishing activation energy, see below.

It should be noticed that the condition $N = 1$ would correspond to glassy AgI, introduced above, rather different from any standard modification; such a glass would have $T_g = 233 \text{ K}$, $\sigma_{298} = 7.16 (\Omega \text{ cm})^{-1}$ (extrapolated above T_g), and vanishing activation energy, $E_{\text{act}} = 0.240 \text{ kcal mol}^{-1}$ ($E_{\text{act}} \approx 7 \text{ kcal mol}^{-1}$ for most glasses studied here). Accordingly, any glass in the present ternary might be described as a solution of such AgI within a homogeneous solvent matrix, where AgI should be thought as completely dissociated, behaving like a "strong electrolyte" in these solutions. This model is to be compared with the quite popular weak-electrolyte theory,^{23,24} where some fraction of the cations are considered as strongly bound to the glassy framework and hence immobile, viz., not all cations are thought to contribute to charge migration.

From the general statement^{21,22} that σ is given by the mobility, μ , times the carrier concentration, n and charge, e , viz.

$$\sigma = \mu ne \quad (15)$$

one should expect for both μ and n an expression like eq 10 might obtain. In the first approximation one may assume that

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$$(\partial\mu/\partial N)_T = 0$$

and further

$$n = \alpha[\exp(\beta)]^N \quad (16)$$

so that the expression

$$\log \sigma = \log A - E_{\text{act}}/2.303RT = \log \mu + \log(\alpha e) + \beta N/2.303$$

would reproduce the form of eq 8. By comparison with eq 6, 7, and 10, after equating powers of N , one obtains

$$\beta = b(10^3)/RT - d$$

or

$$\beta = (10.96 \times 10^3/RT - 3.446) \quad (17)$$

Hence we have for n

$$n = \alpha[\exp(b(10^3)/RT - d)]^N \quad (18)$$

From eq 10 we have

$$\mu = \frac{\exp(c - dN)}{ne} \exp(-(a - bN)(10^3)/RT) \quad (19)$$

and upon rearrangement

$$\begin{aligned} \mu &= \frac{\exp(c)}{ne} \exp((b(10^3)/RT - d)N) \exp(-a(10^3)/RT) \\ &= \frac{\exp(c)}{ne} [\exp(\beta)]^N \exp(-a(10^3)/RT) \end{aligned}$$

and substituting for n using eq 16

$$\mu = \frac{\exp(6.724)}{ae} \exp(-11.2(10^3)/RT)$$

or

$$\mu = \frac{8.32 \times 10^2}{\alpha e} \exp(-11.2 \times 10^3/RT) \quad (20)$$

Finally then, combining eq 17–19, into eq 15 we find

$$\sigma = \frac{8.32 \times 10^2}{\alpha} \exp(-11.2 \times 10^3/RT) \times (3.187 \times 10^{-2})a[\exp(10.96 \times 10^3/RT)]^N = \mu ne \quad (21)$$

From eq 21 values for the conductivity at 298 K have been calculated for all compositions in the present study and are tabulated in Table II. As can be seen from the calculated values, excellent agreement with experimental conductivities are obtained at high equivalent fractions of AgI. In view of the approximation made in the present derivation of a compositionally independent mobility this to be expected. Larger deviations from the experimentally obtained values at small equivalent fractions of AgI may then indicate that indeed the oxyanion framework is playing a large role in the conduction mechanism and would be unaccounted for in the present model.

If we assume $n \approx N\rho$, where ρ is the density ($\rho = 2.5 \times 10^{-2}$ mol cm⁻³, this work), it is possible to obtain a rough estimation of α , viz.

$$\alpha = n[\exp(\beta)]^{-N}$$

hence

$$\alpha \approx 7 \times 10^{-7}$$

where we have used $T = 300$ K and $N = 0.5$. Hence, we finally obtain

$$u = 1.19 \times 10^8 \exp(-11.2 \times 10^3/RT) \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (22)$$

or

$$u/F = 1.23 \times 10^3 \exp(-11.2 \times 10^3/RT) \text{ cm s}^{-1}/V \text{ cm}^{-1} \quad (23)$$

TABLE II

$N(\text{Ag}^+)$	$\log(\sigma_{25}/(\Omega \text{ cm})^{-1})$	
	expt	calcd
AgI + 2Ag ₃ AsO ₄ :AgPO ₃		
0.563	-1.85	-2.241
0.447	-2.387	-3.167
0.364	-2.867	-3.83
0.250	-3.562	-4.74
0.176		-5.331
AgI + Ag ₃ AsO ₄ :AgPO ₃		
0.586	-1.92	-2.057
0.500	-2.02	-2.74
0.368	-2.89	-3.798
0.273	-3.49	-4.556
0.200	-3.94	-5.139
0.143	-4.23	-5.595
AgI + Ag ₃ AsO ₄ :3gPO ₃		
0.600		-1.945
0.486	-2.72	-2.856
0.400	-3.47	-3-4.41
0.100	-4.64	-5.938
0.066		-6.209
0.040		-6.417
0.018		-6.593
0.000	-5.24	-6.736

(where F is the Faraday constant). Choosing $T = 300$ K, we obtain $\mu = 8.5 \times 10^{-6}$ cm s⁻¹/V cm⁻¹ which is not unreasonable for ionically conducting materials.^{25,26}

In light of the above derivations for the mobility μ and number of charge carriers, n , we can discuss more quantitatively the relationship between these properties and their effects upon the bulk conductivity as functions of the composition, N .

Ag Oxyalts as Hosts to "Glassy" AgI? At fixed temperature T , the mobility will be essentially independent of composition in the approximations made here. This can be somewhat justified on the basis of a slowly varying potential field of iodine polyhedra (changing little with the structure of the oxyanion network structure) that the mobile cation "sees" along the conduction path. Hence, the compositional dependence of the conductivity will arise mainly from the number of mobile carriers n . In view of the high polarizability of both Ag⁺ and I⁻, and our data indicating a "strong electrolyte" AgI within these oxide glassy networks, this seems to indicate that there may be anions trapping those Ag⁺ coming from AgPO₃ and Ag₃AsO₄ rendering them immobile. These may very well be oxide sites on the AsO₄³⁻ groups or the phosphate chains.

Additionally this picture implies that, in the case of a single ion hopping mechanism, the Ag⁺ must attain an energy level of 11 kcal mol⁻¹ [for the case $N = 0$, see eq 6] above its rest state to jump into a neighboring available site. Such a large energy well suggests that the ionic jump could be triggered by the surrounding glass matrix. As N increases, cooperative triggering may be effective for neighboring mobile ions, simultaneously activating these ions, eventually reducing the energy barrier to be overcome by each ion. As N approaches unity, the energy well becomes practically null (recall the vanishing $E_{\text{act}} = 0.24$ kcal mol⁻¹ calculated above for $N = 1$), hence the mobile ions no longer need to be triggered; they are like ions of a liquid sublattice, i.e., all of them are engaged in a perpetual translational movement. With the present series of glasses, the room temperature conductivity can be extrapolated to a value significantly larger than that for α -AgI, extrapolated to room temperature (below the $\alpha \rightarrow \beta$ transition of 147 °C). This result coupled with the vanishing activation energy for this fictitious glass indicates the possibility of preparing a glassy solid-electrolyte whose properties are significantly better than the corresponding crystal.

Returning to the wide temperature range Arrhenius plots (Figure 3) of the conductivity, the variation in the slope (activation

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energy) for glasses of highest AgI contents may arise then from this liquidlike behavior of the mobile Ag^+ cations. The data can be (and possibly should be) interpreted as a continuously changing (decreasing) activation energy with increasing temperature describable as a VTF (liquidlike) behavior. An additional measure of this liquidlike sublattice of AgI could be gathered from complex modulus studies (not reported here). Here a temperature-dependent full-width at half-maximum in the electrical modulus loss peak²⁷⁻²⁹ would give an indication to the extent of the liquidlike nature of the mobile cation sublattice by giving information on the temperature dependence of the spectrum of conductivity relaxation times for this sublattice. We envision this temperature dependence in the spectrum of relaxation times to occur from thermally induced structural changes in the liquidlike mobile Ag^+ sublattice. This study is currently being planned for these glasses and to the present authors knowledge remain as yet unpublished.

In very diluted glasses, however, viz. for $N \ll 1$, only few ions could be simultaneously activated and, as N tends to 0, ionic migration would occur via single ion jumps (very different from

the proposed liquidlike behavior of N large). Activation of mobile ions implies that they become able to move along migration pathways, which may be thought tracked in the middle of I^- ions.⁷ The shape of such pathways depends on the structure of the glass matrix; in a naive picture of glass structure, these might be imagined to be like a soft "stuff" just overlying the much more rigid oxyanionic framework which is the main character of the glass, and therefore may be thought as "hard". With increasing N , the "soft" component, viz. the iodide tunnels, becomes significant: eventually, for $N = 1$, it completely replaces the "hard" oxyanionic structure producing a "glassy" AgI described above. Accordingly, one finds that T_g decreases with increasing N . The linear dependence of T_g on N may well arise from a continual softening of the oxyanionic glass network rather than a percolation like softening, though this is not ruled out for N large.

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Theory of the Propagation of Finite Concentration Bands in Gas Chromatography. A Numerical Solution of the Ideal Problem

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The solution of the set of partial differential equations that determines the shape of the elution profile of a finite concentration band in gas chromatography is discussed. It is shown that for the simple case of the elution of a one-component band, in the approximation of the nonlinear, ideal problem, the use of a Godunov scheme permits the design of a computer program which gives an excellent approximation of the elution band profile. In the case of a strong isothermal effect, with n -hexane adsorbed on graphitized thermal carbon black, the comparison between the calculated results and those obtained experimentally shows excellent agreement. At present the most significant source of discrepancy between experimental and predicted profiles is the experimental errors made in the determination of the equilibrium isotherm of the studied compound between mobile and stationary phase, and especially in the determination of the curvature of this isotherm at the origin.

Introduction

The determination of the profile of the elution bands in chromatography is possible in a few restricted cases, essentially when the retention mechanism is simple, the kinetics of exchange between the two phases is rapid, and either the sample size is vanishingly small, in which case the profile is Gaussian, or the sample size is finite but small enough for the equilibrium isotherm to be quantitatively accounted for by a two-term expansion between zero and the maximum concentration of the compound in the mobile phase. In this last case, the band profile is given by an analytical function which exhibits a degree of asymmetry which increases with increasing sample size.^{1,2} Unless the retention is small, the band usually tails and often the decay seems to be exponential, while the front part is close to a Gaussian profile.

This explains why, as a first approximation, the band profile can be represented as an exponentially convoluted Gaussian.³ However, the profile thus obtained is approximate and the modified Houghton equation provides a better model.⁴

These two cases correspond to analytical applications of chromatography and may include instances in which columns are moderately overloaded, as in trace analysis.⁵ When a large sample is introduced in the column, a different situation arises. The approximations made in the derivation of the profiles characterizing the elution of small concentration bands cease to be valid.^{2,5} The profiles obtained do not account for the observations made:

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