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ENTHALPY, VOLUME AND STRUCTURAL RELAXATION IN GLASS-FORMING SILICATE MELTS

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Abstract

Through structural relaxation, the configuration of a viscous liquid changes to allow the Gibbs free energy to be minimum in response to temperature variations. In this review, the practical importance of relaxation in silicate melts is first illustrated by configurational heat capacity and entropy and their connection with viscosity via Adam–Gibbs theory. Relaxation effects on thermal expansion and compressibility are then examined, and the similarity of the kinetics of structural, enthalpy and volume relaxation is pointed out. Turning to microscopic mechanisms, we finally stress the importance of Si–O bond exchange and its decoupling with the motion of network-modifying elements near the glass transition.

Keywords: enthalpy, relaxation kinetics, silicate melts, volume relaxation

Introduction

Silicates have played a key role in glass and relaxation studies. As early as in 1644 Descartes correctly understood that vitrification takes place when the loss of heat makes the constituent particles of a liquid to move slowly enough that their positions are eventually frozen in ‘the figures which they last assumed’ [1]. Silicates then made it possible to discover not only the macroscopic effects of relaxation in 1845 [2], in the case of density, but also the glass transition itself early in the 20th century [3–5].

In fact the glass transition, along with the formation of a disordered solid, signals the loss of internal thermodynamic equilibrium when the time required to adjust the structure of a liquid in response to temperature changes becomes too long with respect to the timescale of the experiment performed. The glass transition thus takes place at higher temperatures for shorter experimental timescales. As a result, the physical properties of glasses depend not only on temperature and pressure, but also on thermal history [6].

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Glass formation in all kinds of viscous liquids has been extensively investigated [7]. Typically, the width of the glass transition range is about 50–100 degrees. It is in this interval that time-dependent properties can be observed macroscopically because the kinetics at which internal equilibrium can be reached is then neither too fast nor too slow. To characterize the rate at which a given property Y gets closer to the equilibrium value Y_e, one defines the relaxation time as

$$\tau_Y = -(Y_t - Y_e)/(\partial Y/\partial t) \tag{1}$$

where Y_t is the value actually measured at instant t.

In Maxwell's treatment of viscoelasticity, the response of a viscous melt to a mechanical perturbation is modeled as that of a spring and a dash pot placed in series. One finds that the relaxation time (τ_η) is given by

$$\tau_\eta = \eta/G_\infty \tag{2}$$

where G_∞ is the shear modulus at infinite frequency of the liquid.

As G_∞ happens not to depend strongly on chemical composition [8], with values of the order of 10 GPa, Eq. (2) indicates that the relaxation time is of the order of 100 s when the viscosity (η) of the liquid is 10^{12} Pa s. Macroscopic property measurements having a typical timescale of 100 s, the glass transition temperature (T_g) is thus operationally defined as the temperature at which $\eta=10^{12}$ Pa s under usual laboratory cooling rates of the order of 10 K min^{-1}.

Particularly during the last decades, much attention has been paid to relaxation mechanisms at an atomic scale [9]. In spite of the considerable natural and industrial importance of silicate melts, however, many aspects of their relaxation have remained little investigated. This situation is due to the experimental difficulties caused by the high temperatures required to investigate silicates, and also to the fact that their relaxation mechanisms are difficult to decipher because their structure is complex and lacks well-defined molecular entities.

Much of the information available for silicates has already been reviewed [8–10]. For lack of space, this paper will thus focus on recent developments with which the author is familiar. A few important consequences of relaxation will first be presented for viscosity and the three basic second-order thermodynamic properties, namely, heat capacity, thermal expansion and compressibility. The kinetics of relaxation for viscosity and first-order properties will then be compared, and a glimpse will finally be given at microscopic mechanisms.

Heat capacity and viscosity

Relaxation is important because the structural changes it induces result in important contributions to the thermodynamic properties of liquids. The heat capacity will be taken as a first example (Fig. 1). Below T_g the heat capacity of glasses (C_{pg}), which is purely vibrational, weakly depends on composition because the glass transition takes place when the Dulong-and-Petit harmonic limit of $3R$/g atom K (R=gas constant) is

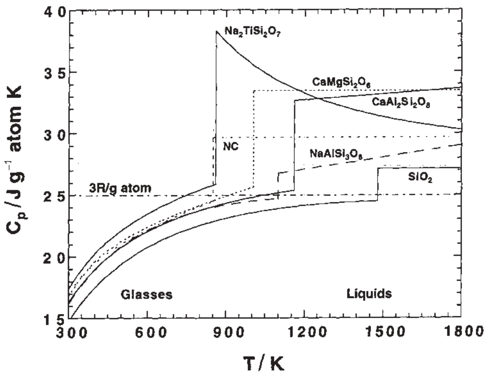

Fig. 1 Heat capacities of various silicate glasses and melts on both sides of the glass transition. Data from [12] for the window glass NC, from [13] for $Na_2TiSi_2O_7$, and data sources listed in [14] for SiO_2, $CaMgSi_2O_6$, $CaAl_2Si_2O_8$ and $NaAlSi_3O_8$

approached [13]. Above T_g, in contrast, the effects of relaxation markedly depend on composition as both the C_p increase and the temperature dependence of the heat capacity of the liquid (C_{pl}) may greatly vary. As justified in detail [14], the relaxational (or configurational) part of the heat capacity may then be written

$$C_p^{conf} = C_{pl} - C_{pg}(T_g) \tag{3}$$

It thus represents the energy needed not to increase the temperature, but to change the structure of the melt, and can be shown to be determined mostly by changes in short-range order in the melt [15].

As will be noted below, short-range order rearrangements also play a major role in viscous flow. Because the close connection between viscosity and glass transition has already been noted, it will not be a surprise to find that viscosity and configurational entropy are also closely related. Now, the simple lattice model of polymers set up by Adam and Gibbs [16] assumes that relaxation times are inversely proportional to the probability of independent structural rearrangements in distinct regions of viscous liquids. On this basis, Adam and Gibbs obtained a result of much wider interest than to polymers only, namely, that τ_η is inversely proportional to configurational entropy (S^{conf})

$$\tau_\eta = A\exp(B_e/TS^{conf}) \tag{4}$$

where A is a pre-exponential term and B_e is approximately a constant proportional to the Gibbs free energy barriers hindering the cooperative rearrangements of the structure.

In a wide variety of contexts, the Adam–Gibbs theory of relaxation processes has received a renewed interest in the last decade [17]. It has proven especially useful for treating quantitatively many features of the viscosity of silicate melts. Because these have already been dealt with in previous reviews [e.g., 18] here we will mention only the temperature dependence. Making use of Eq. (2), we directly obtain from Eq. (3)

$$\log\eta = A_e + B_e / TS^{\text{conf}} \tag{5}$$

where A_e is a constant. Although S^{conf} differs markedly from the entropy difference between silicate liquids and crystals [13], it can be calculated with

$$S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + \int_{T_g}^{T} \frac{C_p^{\text{conf}}}{T}\,\mathrm{d}T \tag{6}$$

With Eq. (6), Eq. (5) is transformed into an expression that has only three fit parameters, A_e, B_e and $S^{\text{conf}}(T_g)$. The remarkable feature is that it reproduces the experimental data (Fig. 2) to within their error margins over more than 13 orders of magnitude [14, 18].

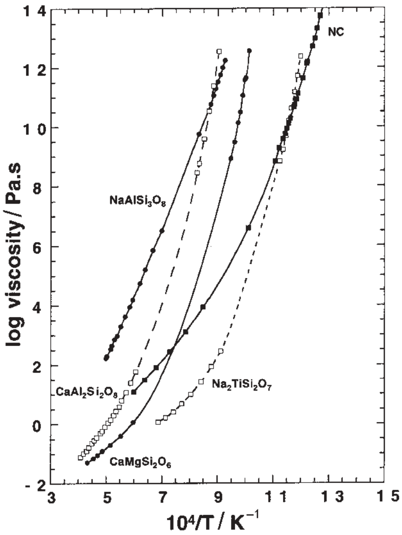

Fig. 2 Viscosity of various silicate melts over wide intervals: experimental data and values calculated with Eq. (5) and the configurational heat capacities derived from the data of Fig. 1 [12, 18, 20]

According to Eq. (5), the deviations of viscosity from Arrhenius laws are determined by the temperature dependence of S^{conf}, and thus by the magnitude of C_p^{conf}. Since the residual entropy of a glass represents the configurational entropy frozen in at the glass transition, one can compare the $S^{\text{conf}}(T_g)$ values determined from Eq. (5) to the residual entropies which can be obtained through calorimetric measurements only if there exists a congruently melting crystalline phase of the same composition [6]. As shown in Fig. 3 by the very good agreement found between these values, the Adam–Gibbs relaxation theory has thus the additional interest of providing a simple and accurate means of determining $S^{\text{conf}}(T_g)$ for complex compositions. To give a sin-

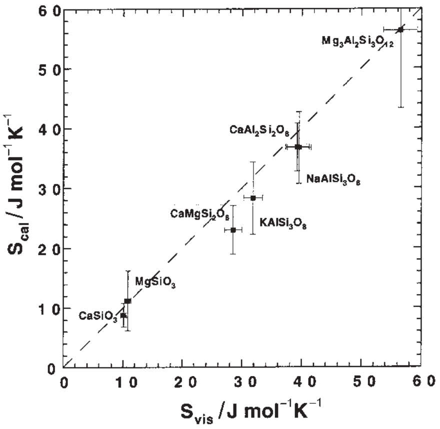

Fig. 3 Comparison between residual entropies of glasses determined from calorimetry and viscosity measurements [18]

gle example, this allows the Gibbs free energy of formation and other thermochemical properties of nuclear waste storage glasses to be determined [20].

The data plotted in Fig. 2 include viscosities higher than 10^{12} Pas. When relaxation times become very long, care must be taken to ensure that equilibrium values are actually obtained. Although time-dependent viscosities are first observed, one can readily check that the same, reversed equilibrium value is measured when starting from temperatures initially higher and lower than the run temperature (Fig. 4). Besides, these measurements conform to general fact that relaxation is non exponential, i.e., that τ_η does not depend only on temperature [21].

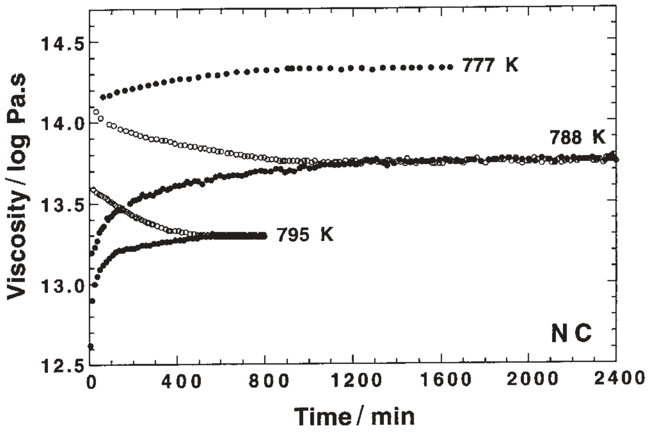

Fig. 4 Viscosity relaxation for NC glass [20] at the temperatures indicated. Increasing viscosities represent relaxation after previous measurements performed at higher temperatures, whereas decreasing viscosities indicate relaxation after annealing at lower temperatures

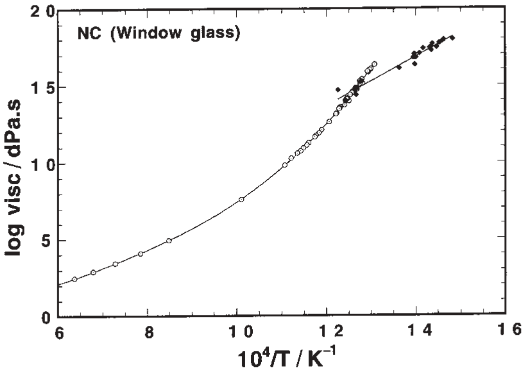

Fig. 5 Viscosity of window glass: equilibrium data ([20], open circles) and viscosity of a sample whose configuration has been frozen in at a temperature of 777 K ([22], solid diamonds). The solid lines represents the values predicted from Eq. (5) with the same A_e and B_e parameters, but with a fixed S^{conf} for the isostructural viscosities [23]

Note finally that if experiments are made fast enough for relaxation not to take place, then the data refer to an unrelaxed, fixed configuration of the material. One then observes a break in the viscosity-temperature curve as shown in Fig. 5 for the window glass NC. Interestingly, Eq. (5) can still be used in that case. Since S^{conf} is constant and refers to the temperature at which the configuration has been frozen,

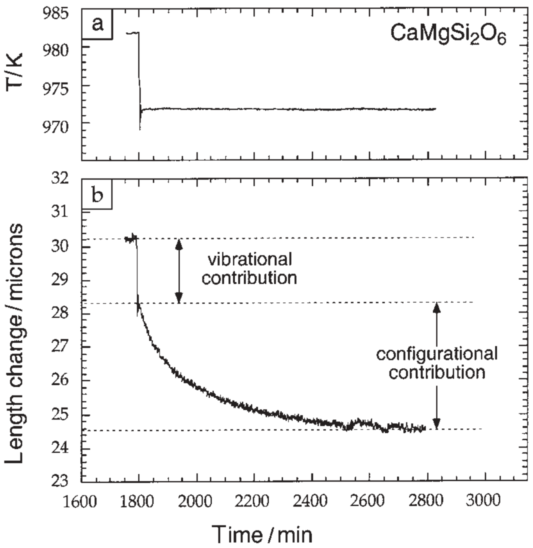

Fig. 6 Volume relaxation as determined in static dilatometry experiments on $CaMgSi_2O_6$ supercooled liquid after a temperature change from 982 to 972 K [27]

Eq. (5) becomes an Arrhenius equation that reproduces the results without the need to introduce any adjustable parameter [23].

Volume relaxation

Although thermal expansion is another important consequence of temperature changes, it is not well enough known particularly close to the glass transition [24, 25] where dilatometry measurements have long shown that it varies considerably. The reason is that, with standard dynamic methods, the thermal expansion coefficient of the liquid (α_l) cannot be determined accurately because relaxation is incomplete over the short temperature interval that can be investigated below the softening point of the sample. Static measurements are thus needed to ensure that relaxation is complete.

Such measurements are possible with a high-precision dilatometer and a well-designed procedure [26]. This is shown in Fig. 6 where the length of a supercooled $CaMgSi_2O_6$ sample is plotted *vs.* time [27]. Since vibrational relaxation is instantaneous, the configurational contribution to thermal expansion may be identified with the curved part of the dilatometric response. The measurements are restricted to temperature intervals of less than 50 K (by too slow kinetics at lower temperatures and sample softening at higher temperatures), but experience shows that α_l can nevertheless determined to better than 5%. Interestingly, they can also be made with the same accuracy on oversaturated water- and CO_2-bearing melts because the kinetics of volatile exsolution remains negligible as long as the viscosity is high [28, 29].

We will make in the next section the comparisons between the kinetics of structural and volume relaxation that are made possible by these observations. Before do-

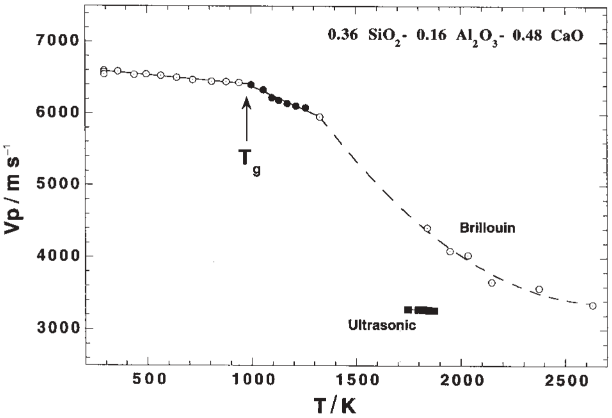

Fig. 7 Effects of structural relaxation on the compressional sound velocity in an aluminosilicate liquid as observed in Brillouin scattering experiments. Note that the shear velocities can no longer be measured after the onset of relaxation, which is apparent near 1500 K, and that complete relaxation leads to the same velocities as measured at lower frequencies by ultrasonic methods [Dung *et al.*, in preparation]

ing so, we turn to another important effect of relaxation which affect determinations of compressibilities. For liquids, the adiabatic compressibility (β_S) is most conveniently determined from measurements of the sould velocity (c) through $\beta_S=1/\rho c^2$, where ρ is the melt density. These measurements are made at MHz frequencies, referring to timescales of the order of 10^{-6} s. The glas transition will thus be observed when the viscosity is only 10^3 Pas, and it is when the viscosity is close to such values that sound velocities depend on frequency [e.g., 30].

Similar observations are made in Brillouin scattering determinations of sound velocities. The timescale of the experiment is then as low as 10^{-11} s so that relaxed β_S values are observed only at viscosities lower than 10^{-2} Pas (Fig. 7). Brillouin scattering is thus generally of little use to measure equilibrium compressibilities, but the very short timescale has the important consequence that shear, and not only compressional, velocities can be measured. Combining both kinds of velocities, one can separate in this way the solid- and liquid-like contribution to β_S, and thus determine what is the contribution of structural changes to the compressiblity [31]. In addition, these measurements directly yield the shear modulus at infinite frequency G_∞ [26] and confirm for silicates that this modulus varies little with temperature and remain in the small 3–32 GPa range of values deduced from other, indirect methods [8].

Relaxation kinetics

Naturally, the question arises to know whether the relaxation kinetics, and thus relaxation times, are the same for different physical properties. As discussed by Moynihan *et al.* [32], this long debated question has to be settled experimentally and could receive different answers for differnet classes of substances. For instance, independently made DSC, viscosity and refractive index measurements have indicated that the relaxation kinetics for enthalpy, viscosity and refractive index are equivalent for the NBS 710 standard boro-

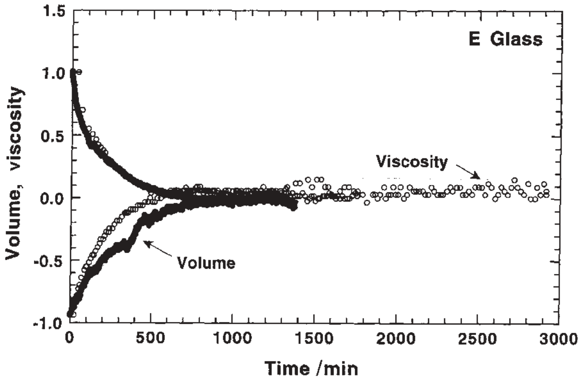

Fig. 8 Volume and viscosity relaxation for E glass at 910 K, after equilibration at 967 K (upper curves) and 900 K (lower curves), in the form of normalized parameters $Y=(Y_t-Y_\infty)/(Y_0-Y_\infty)$ where Y_t, Y_∞ and Y_0 are the values of property Y at time t, at equilibrium, and at time 0, respectively [26]

silicate glass [33]. Likewise, Rekhson *et al.* [34] showed that the viscosity and volume of window glass relax at the same rate. For longer timescales, the same result (Fig. 8) has been found for the calcium borosilicate E glass which is extensively used as a reinforcement fiber [24].

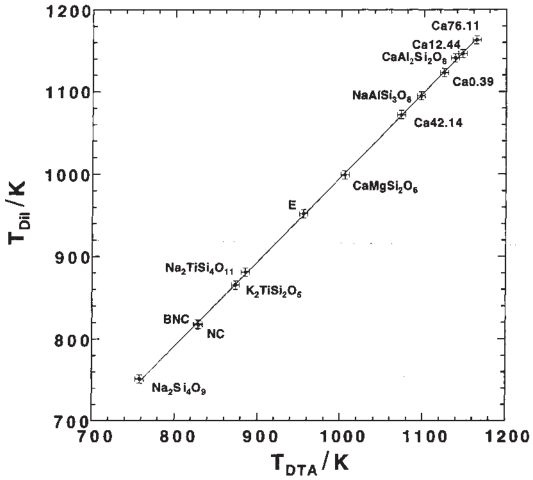

Fig. 9 Linear correlation between the glass transition temperatures of various silicates determined by dilatometry and differential thermal analysis [24]. The E and BNC materials are essentially calcium alumino-borosilicates [20] whereas Ca*x*.*y* designates ternary calcium aluminosilicates with *x* mol% SiO_2 and *y* mol% Al_2O_3

Although such direct observations remain scarce for silicates, there is now a large body of evidence indicating that the equivalence of relaxation kinetics holds true for a very wide range of silicate composition. From independently made viscometry, calorimetry and DSC observations, Webb and Knoche [35] observed a linear correlation between the various glass transition temperatures of a series of silicates and aluminosilicates.

The same conclusion has been arrived at by Sipp and Richet [26] for a wider range of compositions, including boro- and titanosilicates which show anomalous decreases of the heat capacity at high temperature (cf. Fig. 1). By making simultaneous dilatometry and DTA (differential thermal analysis) observations with a newly built apparatus, they observed still better correlations between the viscosity, dilatometry, DTA and drop calorimetry glass transition temperatures (Fig. 9). At the (arbitrarily defined) DTA glass transition temperature, they found for instance that viscosity is nearly constant with an average value of $10^{11.58\ \ 0.11}$ Pas.

From a practical standpoint, an important consequence of the equivalence of relaxation kinetics is that volume relaxation can be modeled from volume measurements or vice-versa. As made by Scherer [36], this allows one to limit the number of parameters needed to model relaxation. In this respect, it must be emphasized that the relation between relaxation times and configurational entropy is valid only at equilibrium. Although experience interestingly shows that the relaxation kinetics are the slowest for supercooled liquids which, like boro- and titanosilicates lose unusually rapidly configurational entropy, there is yet no direct relationship between these relaxation times which govern relaxation far from equilibrium and the equilibrium values [21].

Microscopic *vs.* macroscopic aspects

That the equilibrium structural relaxation time corresponds to the rate of bond exchange with oxygen atoms of the network-forming cations Si and Al has been shown by nuclear magnetic resonance (NMR) measurements [37, 38]. On the other hand, we have seen that τ_η is directly related to the configurational entropy of the melt. As S^{conf} is a bulk property, this indicates that all configurational degrees of freedom are involved in the viscous flow of these liquids. In contrast, a property like electrical conductivity is primarily determined by the motion of only the network-modifier cations. It does not vary as viscosity, especially below the glass transition, and the question thus arises to know how bulk and 'local' transport properties are coupled at high temperatures and become progressively decoupled when the temperature decreases.

For liquid $Na_2Si_3O_7$, available data suggest that relaxation times for Na motion and viscosity are comparable above 1800 K but differ by 10 orders of magnitude at the viscosity glass transition temperature [10]. Similar differences have been evidenced by ^{23}Na and ^{25}Mg NMR experiments on simple sodium and magnesium silicates [40, 41]. These have also shown a contrasting behavior between Na and Mg. Whereas the motion of the latter still appears coupled with viscosity at T_g/T of about 2/3, that of the former is already decoupled at such temperatures. In view of the strong effects of aluminum on melt properties, another important question is to determine whether the charge balance role of alkalis and alkaline earths, which makes the

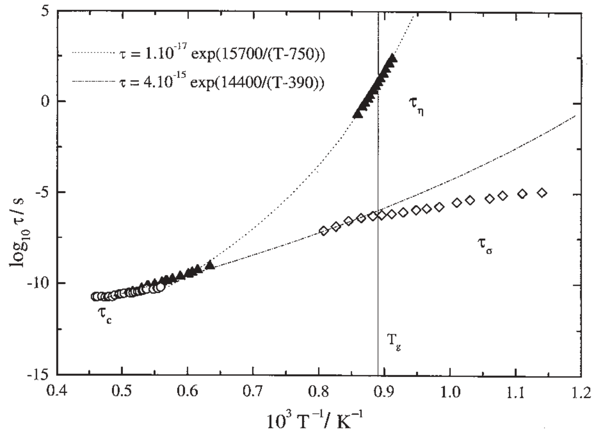

Fig. 10 Relaxation map for a melt with 37 mol% CaO and 27 mol% Al_2O_3 from ^{27}Al NMR (τ_C), viscosity (τ_η) and electrical conductivity (τ_σ) measurements [42]. The glass transition temperature T_g is also indicated

substitution Si/Al possible, affects the mobility of these elements. From other NMR experiments [41], the answer appears to be that Na motion is actually hindered in aluminosilicates with respect to silicates.

As another way of studying these issues, the electrical conductivity of two calcium aluminosilicates has been measured over an unusually large temperature intervals which span the glass and liquid ranges [42]. For both melts, the characteristic time for hopping of Ca^{2+} ions (τ_σ) derived from electrical conductivity were compared with the structural relaxation times determined from viscosity (τ_η) and the ^{27}Al relaxation correlation times observed through static NMR experiments (Fig. 10). At high temperature, the similarity of the three relaxation times indicates that Ca motion is also coupled to viscous flow. Hence, Ca behaves like Mg in the Al-free and aluminosilicates investigated in similar ranges of temperatures [40]. At $T_g/T \sim 2/3$, there thus seems to be little difference in this respect between silicates and aluminosilicates for either Mg or Al.

Near the glass transition, in contrast, the difference between τ_η and τ_σ reaches seven orders of magnitude. This decoupling between calcium motion and bulk relaxation is also illustrated by the change in the conductivity regime at the glass transition. Below T_g, the electrical conductivity becomes much higher than predicted from extrapolation of the liquid values. It follows instead an Arrhenian law, corresponding to the mobility of calcium through the fixed silicate framework of the glass. This change is similar to that reported for the viscosity whereby the non-Arrhenian curve of the fully relaxed liquid transforms to an Arrhenian line at the temperature at which the configuration is fixed (Fig. 5).

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