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On the pressure dependence of the fragility of glycerol

S Pawlus¹, M Paluch¹, J Ziolo¹ and C M Roland²

¹ Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland
² Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342, USA

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Abstract

This work was motivated by ostensibly contradictory results from different groups regarding the effect of pressure on the fragility of glycerol. We present new experimental data for an intermediate pressure regime showing that the fragility increases with pressure up to about 1.8 GPa, becoming invariant at higher pressures. There is no discrepancy among the various literature data taken in toto. The behavior of glycerol is quite distinct from that of normal liquids, a result of its substantial hydrogen bonding.

(Some figures in this article are in colour only in the electronic version)

Although glycerol is one of the most commonly studied vitrifying liquids, it is an atypical glass-former, whose chemical structure changes with T and P due to changes in hydrogen bond concentration. Generally H-bonded materials deviate from the characteristic behavior of liquids [1] and perhaps as a consequence of this complexity, there is a lack of agreement about the influence of pressure on the dynamics of glycerol. One outstanding issue is the effect of pressure (or density) on the temperature dependence of the relaxation times, \( \tau \), or viscosity, \( \eta \). The usual metric of this T-dependence is the fragility or steepness index, \( m \), defined as the apparent activation energy at the glass temperature, \( T_g \), normalized by \( kT \)

\[
m = \left| \frac{d \log x}{dT_g/T} \right|_{T_g},
\]

where \( x \) is \( \tau \) or \( \eta \). For ordinary liquids \( m \) decreases with pressure [2].

Cook et al [3] performed isobaric measurements of the viscosity of glycerol at pressures up to 3 GPa. The data were for temperatures well above \( T_g \); nevertheless, with extrapolations they concluded that \( m \) for \( \eta \) increases with pressure. Paluch et al [4] analyzed high pressure dielectric data from Johari and Whalley [5] and found that for pressures from about 0.7 to 5.5 GPa the fragility is constant, \( \pm 71 \pm 8 \), within the (large) uncertainty. However, this elevated pressure value is larger than determined for atmospheric pressure, \( m = 54 \). (The particular value of \( m \) depends on the definition of \( T_g \) and these correspond to \( \tau(T_g) = 100 \, \text{s} \) ) Comparing the data for \( P = 0 \) and \( P > 0.7 \, \text{GPa} \), the suggestion is that \( m \) must increase with pressure by about 30% over intermediate values of \( P \). However, recently Reiser and Kasper [6] measured dielectric relaxation of glycerol at elevated pressures, reporting that \( m = 53 \) (using \( \tau(T_g) = 100 \, \text{s} \) ) ‘in a good approximation pressure independent up to 700 MPa’. Such a pressure invariance would contradict the results of Cook et al [3] and Paluch et al [4].

To resolve this apparent discrepancy isobaric measurements were carried out on glycerol at both ambient pressure and 1.8 GPa by isobaric cooling. The details of the experimental setup have been described elsewhere [7]. Briefly, the liquid sample and the two electrodes forming a capacitor were placed in Teflon bellows mounted in the high pressure chamber. Force was applied to the piston by means of a hydraulic press, to generate hydrostatic pressure within the chamber. Using this technique, 1.8 GPa pressure could be attained. The temperature was controlled to within 0.5 K by liquid flow from a thermostated bath. Dielectric measurements were performed with a high precision Novo-Control GMBH Alpha impedance analyzer \((10^{-2} - 10^{5} \, \text{Hz})\). The dielectric relaxation times were determined as the inverse of the frequency of the maximum in the loss peak \( (\tau = 1/2\pi f_{\text{max}}) \). The glass temperature was determined as \( \tau(T_g) = 100 \, \text{s} \).

The obtained relaxation times are displayed in figure 1 as a function of \( T_g/T \). There is a marked increase in the
steepness of the data at the higher pressure, with the values of $m$ plotted in figure 2 as a function of pressure. This change in $m$ with pressure corroborates the conclusion that the fragility of glycerol must increase substantially at intermediate pressures, becoming constant only at pressures around 1 GPa or larger.

Collected in figure 2 are all literature results for $m(P)$ of glycerol. The prior $m$ values [4] from the data of Johari and Whalley [5] show an increase of about 30% going from zero to high pressure, consistent with our new results. The fragilities from [6] can be regarded as constant with $P$ within the experimental error, as reported by Reiser and Kasper [6]; however, a systematic increase becomes apparent in figure 2 showing the collected results. Moreover, the results of Win and Menon [8], whose measurements extended to 0.88 GPa (the same pressure range as in [6]), show unambiguously that over this intermediate pressure range, the fragility of glycerol increases to the high pressure value found herein and in [4]. Thus, the dependence of the dielectric relaxation times on pressure is qualitatively the same as that of the viscosity [3].

Some discrepancies among the values of $m$ reported in [4, 6, 8] in their overlapping pressure range is a consequence of the extrapolation procedure applied to the data from [5] during calculation of $m$ in [4]. This is also the source of the larger uncertainties in $m$ than for the fragilities reported in [6] and [8]. Nevertheless, the general agreement with our new result corroborates the increase of $m$ with pressure.

As pointed out above, for normal liquids the fragility decreases with $P$ [2]; the deviation of glycerol from the usual pattern can be ascribed to its hydrogen bonded character [1]. In studying the dynamics near the glass transition, higher pressure measurements are carried out at higher temperatures, making the effect of temperature weaker (smaller apparent activation energy) and thus $m$ smaller. However, for H-bonded liquids the pressure coefficient of $T_g$ is not very large [9], so that the high $P$ experiments do not require substantially higher temperatures. This diminishes the decrease of $m$ with $P$. The increase observed herein at intermediate pressures is more problematic. Although generally one expects pressure to reduce the concentration of directional bonds, molecular dynamics simulations [10] and NMR measurements [11] on glycerol indicate that pressure increases the hydrogen bonding. This is probably due to the fact that the glycerol molecule can form H-bonds at every carbon atom, with the broader distribution of H-bond angles minimizing orientational constraints. A larger $m$ would result from the consequently broadened range of hydrogen bond energies at higher pressure [10].

Deviation from the behavior of unassociated liquids extends beyond the sign of the pressure coefficient of fragility. One general result for normal liquids is that at fixed $\tau$ the shape of the $\alpha$-dispersion is invariant to thermodynamic conditions [12, 13]. However, any changes in chemical structure with $T$ and $P$ change the response function, whereby it is not uniquely determined by the relaxation time [1]. This is observed herein for glycerol (figure 1 inset); the peak does not superpose at constant $\tau$.

In conclusion, new results for glycerol at high pressure together with the previously published data show that its fragility is an increasing function of pressure up to about 1.8 GPa, with $m$ constant at higher pressures. There is no discrepancy in the published results considered in toto, and in fact the behavior of glycerol is as expected for a strongly H-bonded material.

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