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Brief Reports

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Comparison between frequency-dependent specific heat and dielectric relaxation of glycerol and propylene glycol

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The recently developed technique of the frequency-dependent specific heat in the linear-response regime has given useful information on the glass transition, which is supplementary to that obtained by other techniques such as dielectric, ultrasonics, and dynamic light scattering. Previous comparisons of these spectroscopies by Birge and others have reported that the shape of the dielectric loss curves are significantly different from the specific-heat results in glycerol. This has led to speculation of the existence of modes of relaxation that carry entropy but have a very small dipole moment. In this work, we analyze the original glycerol dielectric relaxation data of Howell as well as the dielectric results of Davidson and Cole. We find that the dielectric and specific-heat results for glycerol are in reasonable agreement for both the fractional exponent β of the Kohlrausch-Williams-Watts function and the temperature dependence of loss peak frequencies. The analysis has also been carried out for propylene glycol. However, in this case we find a difference in the values of β for the dielectric and specific-heat results. The dielectric loss peaks are significantly narrower than the peaks from specific-heat spectroscopy.

I. INTRODUCTION

A new technique recently has been developed to measure the frequency dependence of the specific heat in the linear-response regime, over a wide range of frequency, on liquids in thermal equilibrium.[1-3] The technique has been applied initially to two associated liquids, glycerol and propylene glycol,[1,2] and extended to mixtures of O-terphenyl and O-phenylphenol.[3] The quantity measured with specific-heat spectroscopy is not simply the frequency-dependent specific heat $c_p(f)$ but the frequency-dependent product of the specific heat and thermal conductivity, $c_p\kappa(f)$. Most recently, the technique has been extended to decouple the dynamics in c_p and κ such that $c_p(f)$ and $\kappa(f)$ have been measured separately.[3] The dynamic quantity $c_p(f)$ is the linear response of the enthalpy of the equilibrium liquid to a small temperature oscillation at a frequency f. The dependence of $c_p(f)$ on f and how $c_p(f)$ shifts with temperature T offer valuable information on enthalpy relaxation that will be brought to bear on nonlinear and nonequilibrium enthalpy response such as occurring in enthalpy recovery after a temperature step jump. Moreover, it is natural to make comparisons between $c_p(f)$, the dynamic electric polarization, shear and longitudinal compliances. Glycerol is one of the glass-forming liquids that have been studied extensively in relaxations by various other techniques including dielectric, ultrasonics, and dynamic light scattering which include photon-correlation spectroscopy and Brillouin scattering.[4,5] It is interesting to compare the results of the specific-heat spectroscopy with other spectroscopies to see if the shapes of the relaxation function and the temperature dependence of the peak frequencies are the same in all these cases. Such comparisons have been carried out already by Jeong, Nagel, and Bhattacharya,[4] Jeong,[5] and also by Birge[2] for glycerol. These studies conclude that the shapes determined by a number of different experimental probes including $c_p(f)$ (specific-heat spectroscopy), shear modulus $G^*(f)$, and longitudinal modulus $M^*(f)$ (ultrasonics), but excluding dielectric relaxation, are consistent with each other. The dielectric peaks were narrower than any of the others. This was concluded in Ref. 2 by comparing the fractional exponents $\beta_{\rm KWW}$ for the Kohlrausch-Williams-Watts (KWW) fits,

$$\phi(t) = \exp[-(t/\tau_{\rm KWW})^{\beta_{\rm KWW}}] \qquad (1)$$

for the specific heat data and for the dielectric data from Angell and Smith.[6] For specific heat,[2] it has a fractional exponent

$$\beta_{\rm KWW}(c_p) = 0.65 \pm 0.03\,, \qquad (2)$$

while for dipole polarization P (from dielectric relaxation) a significantly larger exponent[2,6]

$$\beta_{\rm KWW}(P) = 0.80 \pm 0.02 \qquad (3)$$

was noted. A similar comparison[2] was made with the exponents β_{DC} for the Davidson-Cole fits[7]

$$\phi(\omega) = (1 + i\omega\tau_{DC})^{-\beta_{DC}} . \tag{4}$$

Again for specific heat,

$$\beta_{DC}(c_p) = 0.51 \pm 0.03 \tag{5}$$

is smaller than

$$\beta_{DC}(P) = 0.58 \pm 0.03 \tag{6}$$

for dielectric polarization, although the difference is not as large as the β_{KWW}'s.

The departure of the shape of dielectric relaxation $\epsilon^*(f)$ from $c_p(f)$ has led to speculations such as the existence of modes of relaxation in liquids that carry entropy but have a very small dipole moment.[2] In this work we analyze the original glycerol dielectric relaxation data of Howell[8] which was the basis for the quote that $\beta_{KWW}(P) = 0.80 \pm 0.02$ [Eq. (3)]. We found instead a width parameter

$$\beta_{KWW}(P) = 0.70 \pm 0.02 \tag{7}$$

from the KWW fits to Howell's data. This new value is significantly smaller than the quoted[2,6] value of 0.80 and brings $\beta_{KWW}(P)$ to better agreement with the value of 0.65 ± 0.03 for $\beta_{KWW}(c_p)$, Eq. (2). Thus, the disagreement between dielectric relaxation and specific-heat spectroscopy is not as significant as previously thought.[2] As a result of this clarification, the accuracy of specific-heat spectroscopy is in effect, enhanced.

II. ANALYSIS OF GLYCEROL DIELECTRIC RELAXATION DATA

Dielectric relaxation of glycerol was investigated by Davidson and Cole[7] and by McDuffie and Litovitz.[9] Unfortunately only the results of the analysis and not the actual data were published. The actual dielectric relaxation data, taken over the frequency range of 0.2 to 2×10^6 Hz from −82.6 to −41.7 °C, has been tabulated by Howell.[8] The dielectric function $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$ is obtained from the tables. In Fig. 1 we plot the dielectric loss ϵ'' vs f for four temperatures. The dielectric data $\epsilon^*(f)$ are then fitted by those calculated from the KWW functions $\phi(t)$ by the Fourier transform

$$\epsilon^*(f) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\int_0^\infty \exp(-i2\pi f t)\left[-\frac{d}{d\tau}\phi(t)\right]dt . \tag{8}$$

The best fits are given by KWW functions with $\beta_{KWW}(P) = 0.70 \pm 0.02$, Eq. (7), and are given by the solid curves in Fig. 1. The peak frequencies for the dielectric loss data of Howell together with those for Im $[c_p\kappa(f)]$ of specific-heat spectroscopy are plotted versus inverse temperature in Fig. 2. Rather good agreement between the two is obtained.

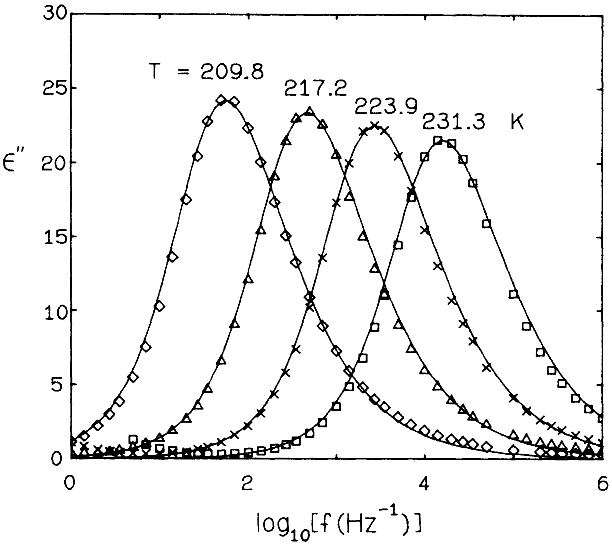

FIG. 1. Dielectric loss $\epsilon''(f)$ spectra for glycerol at various temperatures. Points are from experimental data of Howell (Ref. 8). Solid curves are from calculations based on the KWW function [Eqs. (1) and (8)] with $\beta_{KWW}(P) = 0.70$.

We also compare the present KWW analysis of the dielectric relaxation data of Howell with the Davidson and Cole analysis of the earlier data by the same authors.[7] Even though we do not have the original data by DC, a comparison can be made by using the results of detailed comparisons of the KWW and DC functions by Lindsey and Patterson.[10] The DC parameters β_{DC} and τ_{DC} in Eq. (4) of the Davidson-Cole function that gives a least-squares fit to the complex dielectric function $\epsilon^*(f)$ corresponding to a KWW function with parameters β_{KWW} and τ_{KWW} are related to the latter by numerical relations

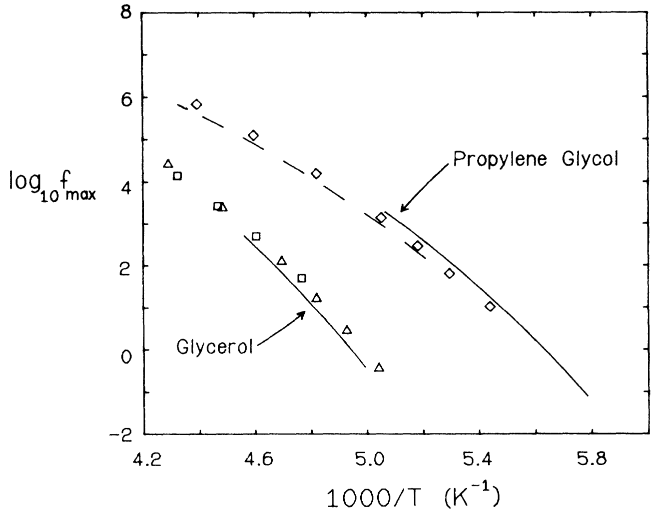

FIG. 2. Dependence of the log (frequency at maximum dielectric loss in Hz) as a function of reciprocal temperature for glycerol and propylene glycol. Squares are from data of Howell. Triangles and diamonds are from Davidson and Cole (Ref. 7) after conversion from τ_{DC} to τ_{KWW} has been made [Eq. (10)]. Solid curves are data from specific-heat spectroscopy. Dashed curve is from dielectric relaxation measurements by Angell and Smith (Ref. 6).

given by Lindsey and Paterson.[10]

$$\beta_{\text{KWW}} = \begin{cases} 0.970\beta_{\text{DC}}+0.144, & 0.2 \leq \beta_{\text{DC}} \leq 0.6\,, \\ 0.683\beta_{\text{DC}}+0.316, & 0.6 \leq \beta_{\text{DC}} \leq 1.0\,, \end{cases} \tag{9}$$

$$\tau_{\text{KWW}} = \tau_{\text{DC}}(1.184\beta_{\text{DC}} - 0.184)\,. \tag{10}$$

Remarkably, via the first of these relations, the value $\beta_{\text{KWW}} = 0.70 \pm 0.02$, deduced for Howell's data by a KWW fit (Fig. 1), corresponds to $\beta_{\text{DC}} = 0.57$, which is the same as the value of 0.566 given by Davidson and Cole[7] for β_{DC} at $-70\,^{\circ}\text{C}$. We use Eq. (10) to convert the τ_{DC}'s (called τ_0 in Ref. 7) to τ_{KWW}'s which enables a comparison of the peak frequencies $f_{\max}$ of both sets of dielectric data[7,8] as well as that of specific-heat spectroscopy to be made (Fig. 2). As can be seen by inspection, there is overall good agreement between these various sets of experimental data. The same has been carried out for propylene glycol (Fig. 2) and again reasonable good agreements are obtained. However, for propylene glycol the disparity of the width parameters for specific-heat and dielectric relaxation remains and appears to be real. From Angell and Smith,[2,6] $\beta_{\text{KWW}}(P) = 0.75$. From Davidson and Cole,[7] $\beta_{\text{DC}}(P) = 0.663$, which corresponds to a $\beta_{\text{KWW}}(P)$ value of 0.77. The two sets of dielectric data are thus in agreement with each other. Compared with $\beta_{\text{KWW}}(c_p) = 0.61 \pm 0.04$, the dielectric loss peaks are significantly narrower than the peaks of the imaginary parts of $c_p\kappa$ from specific-heat spectroscopy.[2]

III. SUMMARY AND CONCLUSION

In this Brief Report we have shown from an analysis of Howell's data that the dielectric data of glycerol has width exponent $\beta_{\text{KWW}}(P)$ quite comparable to $\beta_{\text{KWW}}(c_p)$ from specific-heat spectroscopy. Previous reports of a significant discrepancy between the two are actually not valid due to using an incorrect value of $\beta_{\text{KWW}}(P)$ of 0.80 ± 0.02 instead of 0.70 ± 0.02. Thus, there is really no significant discrepancy. However, the large discrepancy between $\beta_{\text{KWW}}(c_p)$ and $\beta_{\text{KWW}}(P)$ for propylene glycol appears real. It would be of interest to explore such possible differences in β in a wider class of glass-forming liquids.

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