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# Consequences of applying Scaife's remarks to the dielectric relaxation data for glycerol

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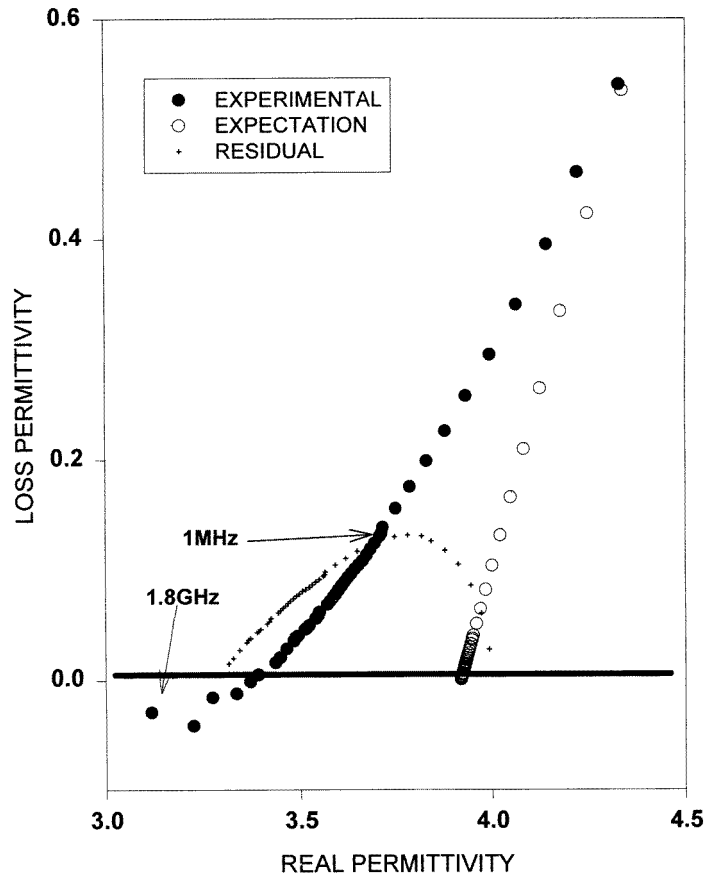
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**Abstract.** One of the early works on the dielectric properties ( $\varepsilon(\omega)$ ) of glycerol was by Davidson and Cole (Davidson D W and Cole R H 1951 *J. Chem. Phys.* **19** 1484) who proposed a new relaxation function that is currently used to represent dielectric relaxation behaviour. Deviations from the expected high-frequency linear behaviour in a complex-plane plot were interpreted in terms of a second high-frequency relaxation process. Somewhat after the Davidson and Cole paper, Scaife (Scaife B K P 1963 *Proc. Phys. Soc.* **81** 124) suggested that instead of analysing dielectric data in terms of the real and imaginary coordinates of the complex relative permittivity  $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$  as in the Cole–Cole plot, one should use the real and imaginary coordinates of the function  $\rho(\omega) = (\varepsilon(\omega) - 1)/(\varepsilon(\omega) + 2)$ , which is proportional to the complex polarizability of an isolated dielectric sphere. This suggestion was made because, in a dielectric sphere, long-range dipole–dipole coupling vanishes and because a better weighting is given to individual relaxation processes. In this  $\rho(\omega)$  representation, the deviations observed at high frequencies disappear and there is no longer any need to postulate a high-frequency relaxation process. The recommendations by Scaife have been largely ignored and these high-frequency deviations continue to receive considerable attention from many investigators. It is the object of this work to apply the recommendations of Scaife to current dielectric relaxation data for glycerol which now span a much broader and higher frequency range, i.e.  $10^{-2}$  to  $10^9$  Hz. The deviations are no longer present when his recommendations are followed. It is expected that these observation will have important consequences for current theoretical models for dielectric relaxation.

## 1. Introduction

A literature search by the authors on the molecular or relaxation dynamics of glycerol found at least 90 citations since 1977. Prior to 1977 a literature search is more difficult to conduct but that time period also contains some very important papers on glycerol. Glycerol has been an object of study for a long time for at least two reasons. First, the molecule has three hydroxyl groups and this enables the system to form an extensive network through hydrogen bonding. Second, measurements can be made well below its freezing point because the material supercools. Of the various early papers on glycerol, one significant one is by Davidson and Cole [1] who reported a new relaxation function for representing dielectric relaxation data. They reported deviations from this assumed (linear) high-frequency behaviour in the complex plane and interpreted them in terms of a second high-frequency dispersion.

Another important early paper was by Scaife [2] who questioned the utility of analysing dielectric relaxation data solely in terms of the complex permittivity ( $\varepsilon(\omega)$ ). His arguments,

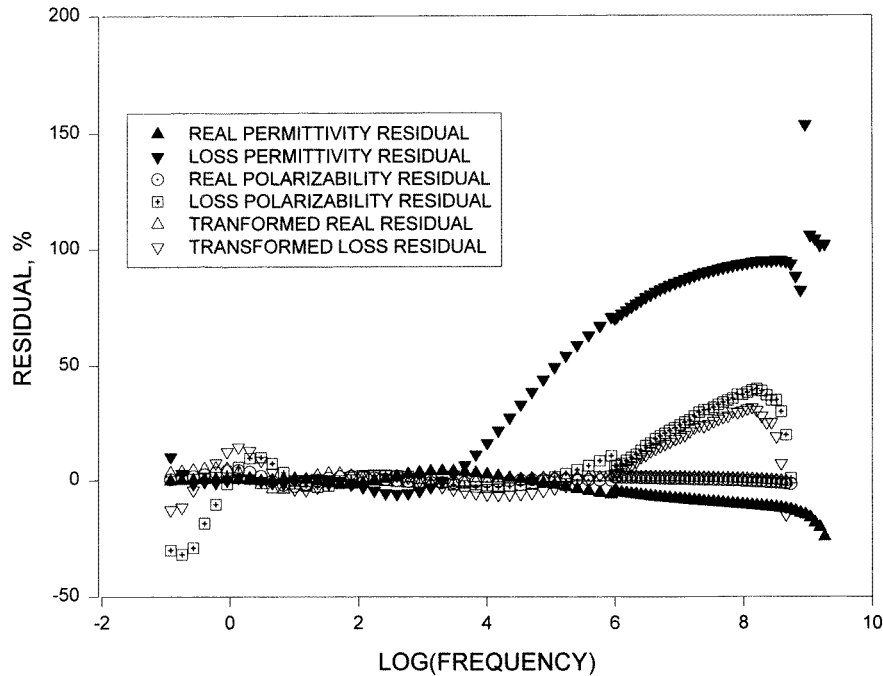


**Figure 1.** The high-frequency region of the complex-plane plot for glycerol  $\varepsilon(\omega)$  data at 203 K. The key identifies the experimental and expectation values and their difference, i.e. the residual. 3.8 was added to the real residual as an estimate of the high-frequency limit of the alpha process.

based on the relative weighting of various regions of the dielectric process, led him to suggest that it is the complex polarizability,  $\rho(\omega)$ , that should be used for analysing dielectric relaxation data. The quantity  $\rho(\omega)$  is proportional to the complex polarizability of a dielectric sphere suspended in a vacuum to which an electric field is applied and is related to  $\varepsilon(\omega)$  by means of equation (1):

$$\rho(\omega) = \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2}. \quad (1)$$

In this expression,  $\varepsilon(\omega)$  is the complex permittivity measured at the angular frequency  $\omega = 2\pi f$  where  $f$  is in Hz. The real part of this expression is denoted by  $\varepsilon'(\omega)$  while the imaginary part is denoted by  $\varepsilon''(\omega)$ . These parts are related to the complex dielectric constant through the expression  $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$  where  $i$  is  $\sqrt{-1}$ . Similar definitions exist for  $\rho(\omega)$ . According to Scaife, when the dielectric dispersion data for glycerol are analysed in terms of  $\rho(\omega)$ , these high-frequency deviations in the complex plane are no longer present. In other words the existence of a high-frequency dispersion depends on the method of data representation, and hence its reality is suspect. Scaife's suggestion is important because glycerol is receiving considerable attention and these deviations continue

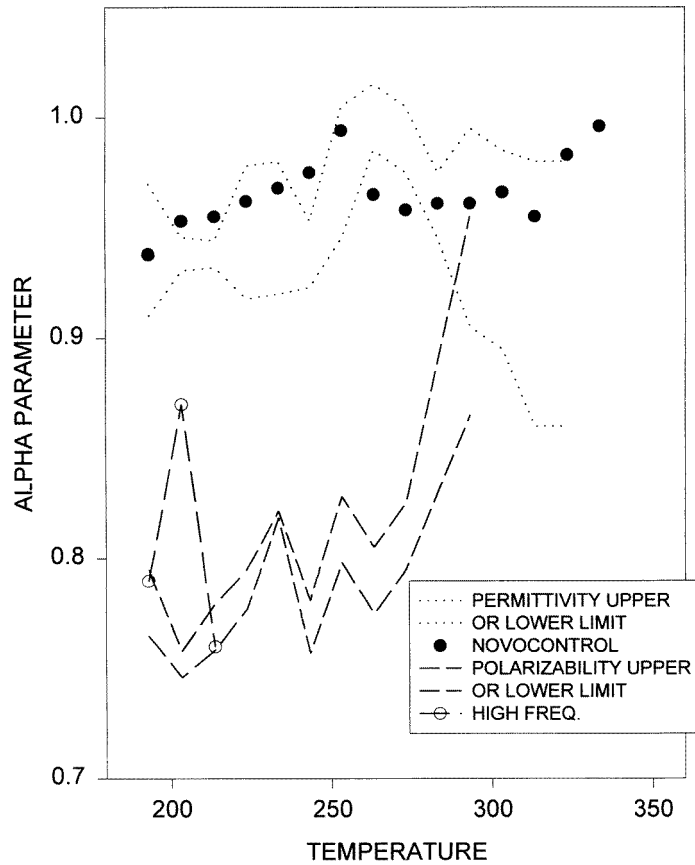


**Figure 2.** A plot of  $r(\omega)$  and  $r''(\omega)$  defined by equations (3) and (4) as functions of  $\log(\text{frequency})$  for the various methods of data representation defined in the text for glycerol at 203 K.

to be observed and interpreted [3] in terms of a high-frequency relaxation process. The object of this work is to examine dielectric relaxation data for glycerol in the manner of Scaife, but using data which now cover a frequency range that extends three decades higher—that is, to  $10^9$  instead of  $10^6$  Hz.

## 2. Experimental data

The dielectric measurements used in this work were supplied to the authors by NOVOCONTROL [4]. The measurements were made over a frequency range of  $10^{-2}$  to  $1.8 \times 10^9$  Hz and a temperature range of 193.2 to 333.2 K in 10 K increments. The temperature control is stated to be within  $0.5^\circ\text{C}$  with a cycle time of about five minutes. The measuring equipment and cells are changed at a frequency of 1 MHz. Close inspection of the data in the vicinity of the changeover frequency, which is necessary for this study, reveals a small discontinuity. Discussions with NOVOCONTROL personnel revealed that this discontinuity is due to small percentage errors in the determination of the cell constant. In addition there are some stray corrections and lead corrections. Prior to the adjustments, there was a discontinuity of about 0.02 loss units and 0.04 real units at 1 MHz. Eliminating the discontinuity, by adjusting the cell constant accordingly, has mostly a cosmetic effect, because making the corrections in the analysis of the data has only a small effect on the parameters and no effect on the conclusions. We present here the results obtained using data that were corrected. The data at each temperature were fitted to a relaxation [5, 6]



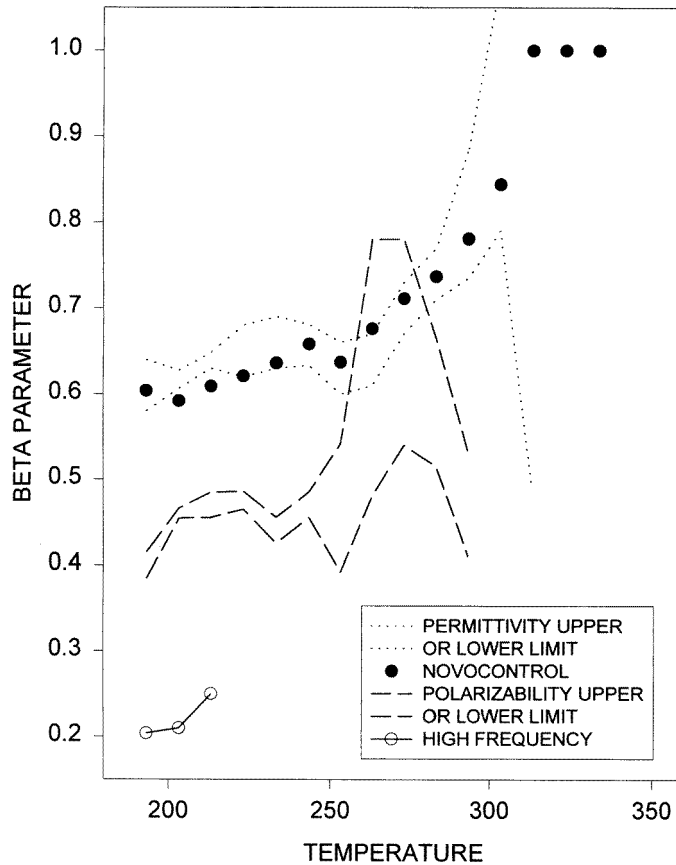
**Figure 3.** A plot of the parameter  $\alpha$  against temperature for the various methods of representing the dielectric relaxation data for glycerol defined in the key. The upper and lower limits are the estimated values for  $\alpha \pm 1.5\sigma$ , where  $\sigma$  is the parameter confidence interval. 'HIGH FREQ.' refers to the parameter  $\alpha$  for the high-frequency process shown in figure 1.

function defined as

$$\frac{\varepsilon(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \{1 + (i\omega\tau_0)^{\alpha}\}^{-\beta}. \quad (2)$$

It is relatively straightforward [5, 6] to show that  $\varepsilon_0$  is the static or equilibrium permittivity,  $\varepsilon_{\infty}$  is the instantaneous permittivity and  $\tau_0$  is the relaxation time. Often, the relaxation frequency is used and is defined as  $f_0 = 1/\tau_0$ . The parameter  $\alpha$  represents the width and  $\beta$  represents the skewness of the relaxation process. The Davidson and Cole expression is obtained when  $\alpha$  is set to unity in equation (2). There are two interesting analytical features of equation (2). The first is that in a complex-plane plot the limiting high-frequency behaviour is a straight line. The second is that both the low- and high-frequency limiting slopes of a  $\log(\text{loss})$  versus  $\log(\text{frequency})$  plot are linear. The low-frequency slope is equal to  $\alpha$  while the high-frequency slope is equal to  $-\alpha\beta$  for these  $\log(\text{loss})$  versus  $\log(\text{frequency})$  plots.

Estimation of the five parameters of equation (2) using non-linear regression techniques has been fully discussed [7–10]. These methods can also be used to estimate parameter



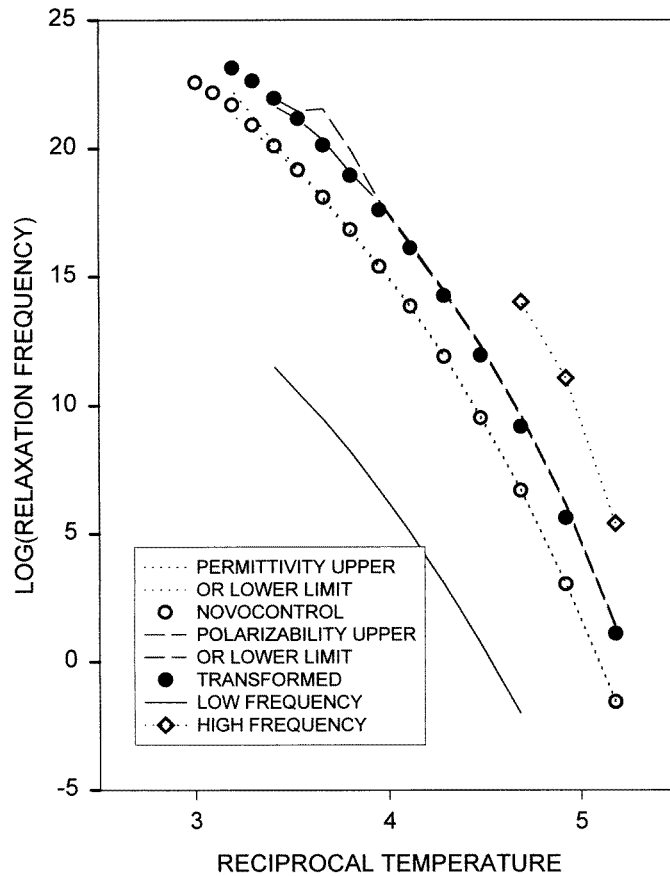
**Figure 4.** A plot of the parameter  $\beta$  against temperature for the various methods of representing the dielectric relaxation data for glycerol defined in the key. The upper and lower limits as well as 'HIGH FREQUENCY' are defined in the caption of figure 3.

confidence intervals ( $\sigma$ ) so comparisons with the parameters from NOVOCONTROL or other studies can be made on a sound statistical basis. Transformation of  $\varepsilon(\omega)$  data to  $\rho(\omega)$  data exaggerates experimental errors, and the confidence intervals may appear to be unduly large. Briefly, the major sources of high model standard errors in the estimates and consequently also the parameters and their confidence intervals are the temperature cycling and its effect on the relaxation time; see section 3 in reference [9].

### 3. Results and discussion

#### 3.1. Dielectric permittivity and high-frequency relaxation

Davidson and Cole (see figure 5 in reference [1]) gave a complex-plane plot of  $\varepsilon'(\omega)$  for glycerol at 203 K to illustrate the high-frequency deviations from the predicted linear behaviour in a complex-plane plot. The measurements by Davidson and Cole were only made up to 5 MHz. Shown in figure 1 of this work is a similar plot for the same temperature (203 K) but using data up to 1 GHz. Except for the change of notation given below, the



**Figure 5.** A plot of the parameter  $\ln(f_0)$  against temperature for the various methods of representing the dielectric relaxation data for glycerol defined in the key. The upper and lower limits are defined in the caption of figure 3.

resulting behaviour is the same as that noted by Davidson and Cole. The loss for the four highest-frequency points is negative; we assume this to be due to experimental error and these data will be deleted from all further consideration.

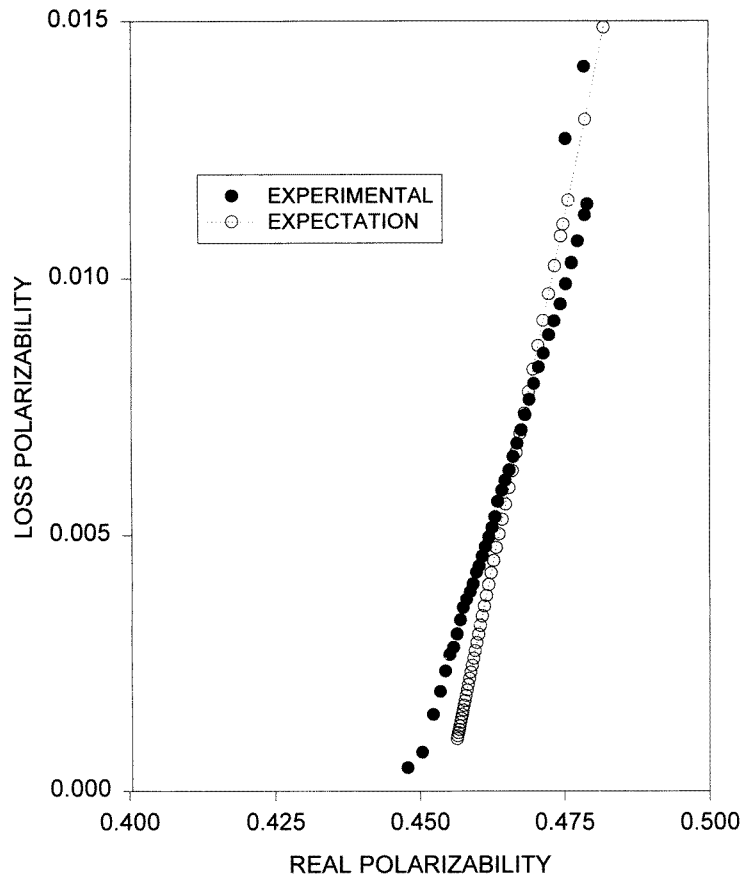
We define real,  $r'(\omega)$ , and loss,  $r''(\omega)$ , percentage residuals as

$$r'(\omega) = 100 \times \frac{\varepsilon'(\omega) - \varepsilon'_e(\omega)}{\varepsilon'(\omega)} \quad (3)$$

with a similar expression for  $\varepsilon''(\omega)$ , namely

$$r''(\omega) = 100 \times \frac{\varepsilon''(\omega) - \varepsilon''_e(\omega)}{\varepsilon''(\omega)}. \quad (4)$$

In these expressions the subscript  $e$  represents the expectation values determined from equation (2). Plots of the real and loss percentage residuals as functions of  $\log(\text{frequency})$  are given in figure 2. They are identified as the real permittivity residual and the loss permittivity residual in the key. There are significant deviations in the percentage residuals at frequencies above  $10^4$  Hz. A complex-plane plot of the residuals after 3.8 has been

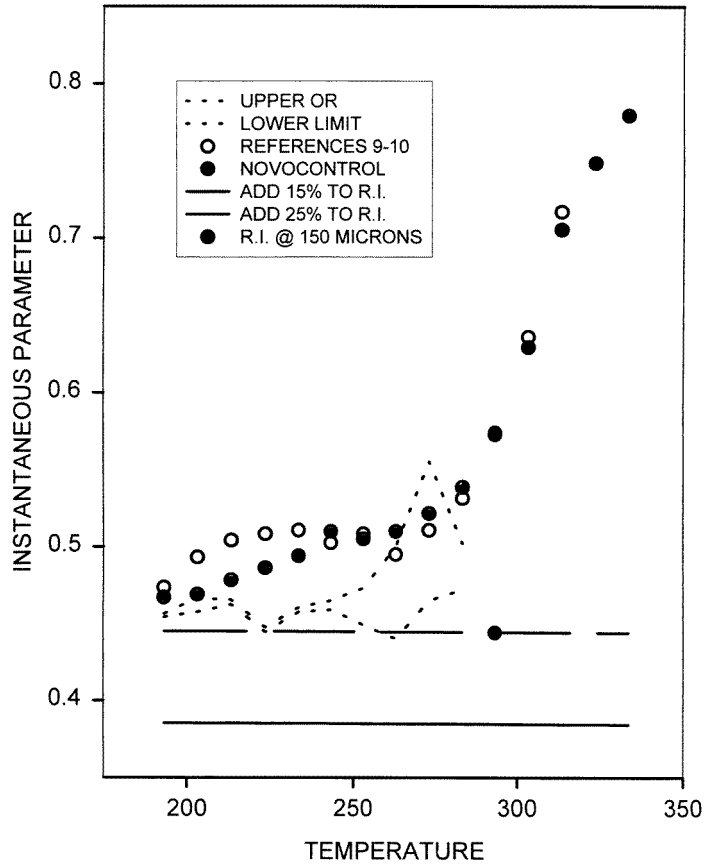


**Figure 6.** The high-frequency region of the complex-plane plot for glycerol  $\rho(\omega)$  data at 203 K. The key identifies the sources of the data.

added to the real residual is given in figure 1. The line represents the results of fitting the residuals to equation (2).

This method of analysis was extended to  $\varepsilon(\omega)$  data for all the available temperatures. The results for the parameter  $\alpha$  at different temperatures are given in figure 3. In this figure the NOVOCONTROL parameters are represented by the filled circles. The dotted lines represent  $\pm 1.5\sigma$  determined by the methods discussed in references [6–9]. The parameter  $\alpha$  for the high-frequency process is represented by the unfilled circles (there are three). The high-temperature data poorly define the high-frequency side of the relaxation process. Under these conditions the high-temperature data could only be regressed when we greatly relaxed our convergence criterion. For this reason the parameters at the highest temperatures are not reported. Also, as is apparent from figure 3, the confidence intervals increase with temperature for  $\varepsilon(\omega)$  parameters. This is because as the temperature increases the relaxation process shifts to higher frequency and the available frequency range does not completely define the relaxation process. The results for the parameter  $\beta$  are given in figure 4. The symbols in this figure have the same meaning as they do for  $\alpha$  in figure 3. The important observation in figures 3 and 4 is that the parameters  $\alpha, \beta$  for the high-frequency process can be represented by equation (2) and not one of its limiting forms; that is,  $\alpha, \beta \neq 1$ . The



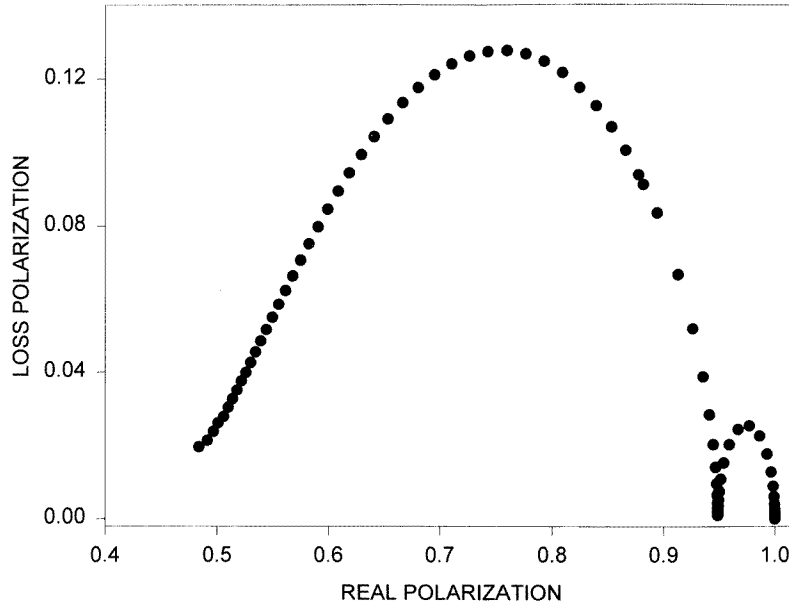


**Figure 7.** A plot of  $\rho_{\infty}$  against temperature derived from the various methods of representing the dielectric relaxation data for glycerol. The upper and lower limits represent  $\pm 1.5\sigma$  for  $\rho_{\infty}$  estimated from  $\rho(\omega)$  data. Quantities labelled as coming from references [9, 10] or NOVOCONTROL signify values of  $\rho_{\infty}$  calculated from  $\varepsilon_{\infty}$ . In each case,  $\varepsilon_{\infty}$  was first determined from  $\varepsilon(\omega)$  data and then equation (6) was used to calculate  $\rho_{\infty}$ . The two solid lines and the solid circle on a broken line represent  $\rho_{\infty}$  estimated from equation (5) using different values for the refractive index as described in the text.

results for the temperature dependence of  $\ln f_0$  are given in figure 5. The lines and symbols have the same significance as they do in the previous figures.  $\ln f_0$  for the high-frequency process appears to parallel that for the low-frequency process.

### 3.2. Complex polarizability

The complex polarizability is calculated from  $\varepsilon(\omega)$  using equation (1). A complex-plane plot of the polarizability for the same temperature and frequency ranges as are shown in figure 1 is given in figure 6. These results show that there may be systematic deviations between the experimental and fitted values in this frequency range; they are much smaller and of a different type. What is important to note is that the experimental high-frequency complex-plane plot is linear. The results obtained for  $r'(\omega)$  and  $r''(\omega)$  using the experimental and fitted values of  $\rho(\omega)$  are given in figure 2 and labelled as real or loss polarizability residuals.



**Figure 8.** A complex-plane plot of  $\rho(\omega)$  for glycerol at 233 K. The low-frequency dispersion observed in this figure is the 'dc tail' often observed in complex-plane plots of  $\varepsilon(\omega)$  data where the conductivity is significant.

The quantities  $r'(\omega)$  and  $r''(\omega)$  calculated from the fitted values of  $\rho(\omega)$  and the inverse of equation (1) are also plotted in figure 2. The loss residual for the  $\rho(\omega)$  representation has been reduced by a factor of 2.5 while the real residual has been reduced by an order of magnitude so that it is now similar at low and high frequencies. These residuals could not be analysed in terms of a high-frequency relaxation process as was done for the  $\varepsilon(\omega)$  data.

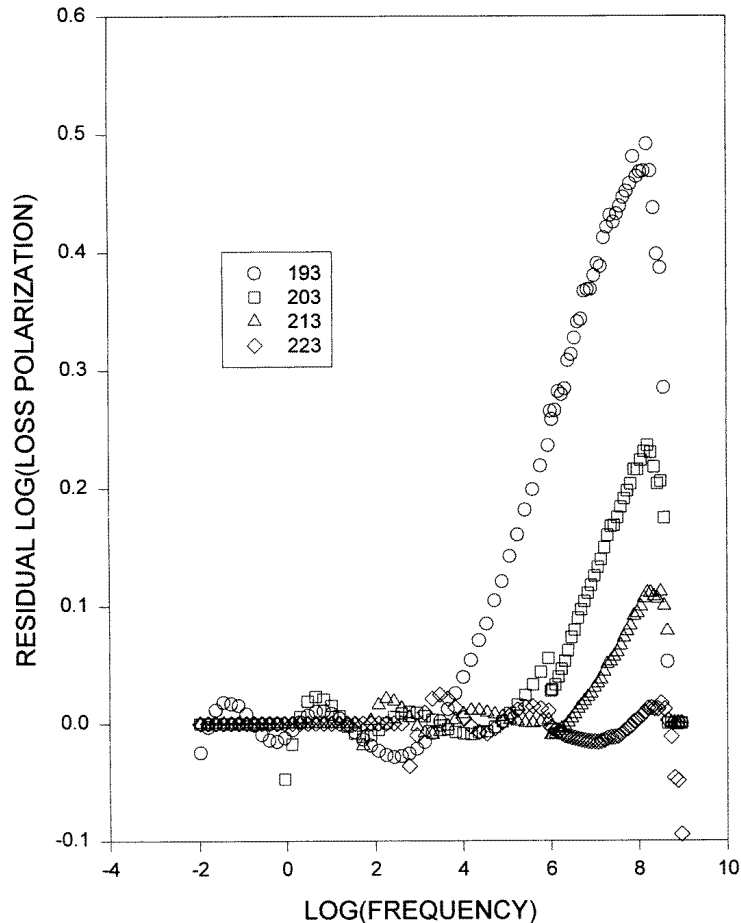
A plot, for the  $\rho(\omega)$  data, of  $\alpha$  against temperature is given in figure 3, of  $\beta$  against temperature in figure 4, of  $\ln f_0$  against temperature in figure 5, and of  $\rho_\infty$  against temperature in figure 7. The equilibrium parameter,  $\rho_0$ , is well behaved and need not concern us here. In addition, the values of  $\rho_\infty$  calculated from the Havriliak–Negami parameters for the  $\varepsilon(\omega)$  data are included.

A complex-plane plot of  $\rho(\omega)$  data at 233 K is given in figure 8. The low-frequency dispersion is due to the dc tail observed in  $\varepsilon(\omega)$  plots. The temperature dependence of the relaxation time is given in figure 5.  $\alpha = \beta = 1 \pm 0.02$  while  $\Delta\rho = \rho_l - \rho_h \approx 0.05 \pm 0.0001$ , where the subscripts refer to the high- and low-frequency limits of the relaxation process.

### 3.3. The temperature dependence of $\rho_\infty$

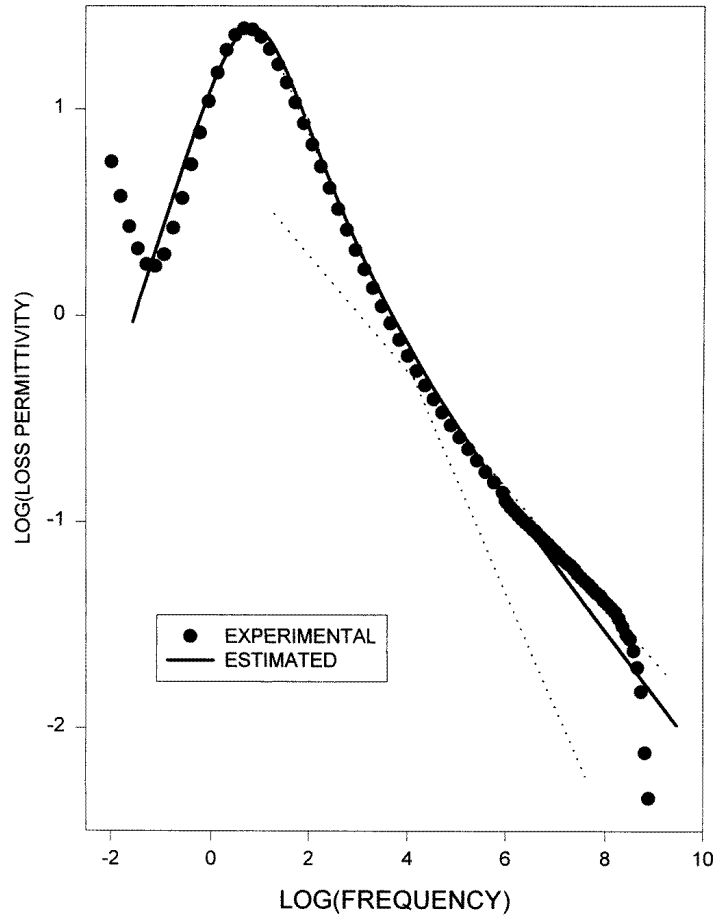
The temperature dependence of  $\rho_\infty$  calculated from  $\varepsilon_\infty$  is anomalous. We can estimate the temperature dependence of  $\rho_\infty$  from the Clausius–Mossotti [11] equation, i.e.

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = \frac{4\pi N}{3} \alpha_0 = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \frac{M}{d} \quad (5)$$



**Figure 9.** A plot of  $\log(\text{loss permittivity residual})$  versus  $\log(\text{frequency})$  for the temperatures (in K) listed in the key.

where  $n^2$  is the square of the refractive index at very low (optical) frequencies,  $M$  is the molecular weight,  $d$  is density and  $\alpha_0$  the polarizability of the molecule. The temperature dependence of  $n$  is due to the temperature dependence of  $d$  since all of the other quantities in equation (5) are independent of temperature. The assumption is made that at very low optical frequencies,  $n^2 \rightarrow \epsilon_\infty$  at very high frequencies. What is needed to solve this problem is an estimate of the refractive index and some allowance for the atomic polarizability, normally taken to be about 15% on  $n$ , and the temperature dependence of the density. We take the refractive index of glycerol to be  $n(20^\circ\text{C}) = 1.476$  [12] and allow 15% for atomic polarizability. We calculate the density dependence in the following way. We assume that glycerol can be treated as a polymer with the repeating unit  $(\text{HCOH})_3$  and use the method described by Van Krevelen and Hoftyzer [13]. The Van der Waals volume  $V_w$  is calculated to be  $54 \text{ cm}^3$ . The results of the calculation are given in figure 7. Cartwright and Errera [14] reported the refractive index in the far-infrared, i.e. in the range  $50$  to  $150 \mu\text{m}$ , to be  $3.5$  at room temperature. The results of using this value for  $n$  in equation (5) are given in figure 7. The instantaneous parameter calculated from the regression of  $\epsilon^*(\omega)$  data shows



**Figure 10.** A plot of  $\log(\epsilon''(\omega))$  versus  $\log(\text{frequency})$  for glycerol at 203 K. The experimental data as well as the quantities calculated from equations (2) and (6) are identified in the key. The straight dotted lines are drawn in accordance with the method of Lunkenheimer *et al* [3].

an anomalous temperature dependence. This comes about because of the deviations at high frequencies. As the temperature is increased, the data shift to the low-frequency portion of the process and away from the high-frequency deviations.

#### 3.4. Plots of $\log(\text{loss})$ versus $\log(\text{frequency})$

Recently, dielectric relaxation data have been represented as  $\log(\text{loss})$  versus  $\log(\text{frequency})$  plots because the loss can be measured over several decades with nearly the same experimental error, i.e. percentage experimental error. In plots of  $\log(\rho''(\omega))$  versus  $\log(f)$ , small deviations are observed at high frequencies. A plot of the residuals, i.e.  $\log(\text{experimental expectation})$  against  $\log(\text{frequency})$ , is given in figure 9. In these plots a loss maximum is well defined, rather than there being an increasing systematic deviation from high-frequency linear behaviour, as was observed by Lunkenheimer *et al* [3]. The loss maximum also decreases rapidly with temperature. Furthermore, the loss maximum frequency appears to be independent of temperature. Analysis of the linear loss

residuals and the imaginary part of equation (2) yields  $\Delta\rho = 0.00442 \pm 0.00008$  and  $\alpha \simeq \beta = 0.95 \pm 0.05$  for  $T = 193$  K. Although an interpretation of this loss peak is uncertain, it is not similar to those reported by Lunkenheimer *et al.*

We can calculate  $\varepsilon(\omega)$  from equation (2), and the parameters used to represent the experimental  $\rho(\omega)$  data and the inverse of equation (1), i.e. equation (6):

$$\varepsilon(\omega) = \frac{2\rho(\omega) + 1}{1 - \rho(\omega)}. \quad (6)$$

The results of this calculation are given in figure 10. In order to understand this behaviour it is important to recognize that as reported by Scaife [2] the transformation of  $\varepsilon(\omega)$  to  $\rho(\omega)$  data or the inverse is a bilinear transformation. This means that a straight line in one representation may be a curve in the other representation. Inspection of the calculated values of  $\varepsilon(\omega)$  in figure 10 shows that there are two approximately linear regions represented by dotted lines in that figure.

#### 4. Conclusions

Deviations from linear high-frequency behaviour for glycerol either in a complex-plane plot or in a  $\log(\varepsilon''(\omega))$  versus  $\log(\text{frequency})$  plot have received considerable attention. None of the discussions included Scaife's suggestion. When Scaife's suggestion is followed, these high-frequency deviations disappear. The questions that we are confronted with are listed below.

(1) What is the significance of a relaxation process that depends on the method of data representation?

(2) What do these observations mean in terms of dielectric theories that conclude that molecular and macroscopic relaxation times are similar?

The answer to the first question is simple: the significance of the high-frequency relaxation process is nil. The second question is of considerable theoretical importance for polar liquid theory, because it implies that conclusions based on Glarum's [15] or Cole's [16] correlation function theories are incorrect, while Scaife's views are correct.

#### Acknowledgments

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#### References

- [1] Davidson D W and Cole R H 1951 *J. Chem. Phys.* **19** 1484
- [2] Scaife B K P 1963 *Proc. Phys. Soc.* **81** 124
- [3] These deviations have been commented on by many investigators; see for example Lunkenheimer P, Pimenox A, Schiener B, Bohmer R and Loidi A 1996 *Europhys. Lett.* **33** 611
- [4] See figure 4 in the April 1996 issue of the *Dielectric Newsletter* produced by NOVOCONTROL GmbH, Oberebacher Strasse 9, D-56414 Hundsangen, Germany.
- [5] Havriliak S Jr and Negami S 1966 *J. Polym. Sci. C* **14** 99
- [6] Havriliak S Jr and Negami S 1967 *Polymer* **8** 161

- [7] Havriliak S Jr and Watts D J 1986 *Design, Data and Analysis: By Some Friends of C Daniels* ed E Mallows (New York: Wiley)
- [8] Havriliak S Jr and Watts D J 1986 *Polymer* **27** 1509
- [9] Havriliak S Jr and Havriliak S J 1993 *J. Mol. Liq.* **56** 49
- [10] Havriliak S Jr and Havriliak S J 1996 *Dielectric and Mechanical Relaxation in Materials* (New York: Hanser) ch 3
- [11] Böttcher C J F, Van Belle O C and Rip A 1973 *Theory of Electric Polarization* vol 1 (New York: Elsevier Scientific) ch 5, pp 172–173
- [12] *CRC Handbook of Chemistry and Physics* 1957 74th edn (Cleveland, OH: Chemical Rubber Company Press)
- [13] Van Krevelen D W and Hoftyzer P J 1976 *Properties of Polymers* (New York: Elsevier Scientific)
- [14] Cartwright C H and Errera J 1936 *Proc. R. Soc. A* **154** 138
- [15] Glarum S H 1960 *J. Chem. Phys.* **33** 1371
- [16] Cole R H 1965 *J. Chem. Phys.* **42** 637