

# Test of the fractional Debye-Stokes-Einstein equation in low-molecular-weight glass-forming liquids under condition of high compression

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From temperature studies at ambient pressure, it was pointed out for several glass-forming liquids that the  $\alpha$ -relaxation time ( $\tau$ ) can be related to the dc-ionic conductivity ( $\sigma$ ) through the phenomenological fractional Debye-Stokes-Einstein (DSE) equation. In the present paper we test the validity of fractional DSE equation for relaxation data obtained from pressure variable experiments. To this end we carried out broadband dielectric measurements (10 mHz–10 MHz) in a wide range of pressures (0.1–300 MPa). The material under study were *N,N*-diglycidyl-4-glycidyoxyaniline and *N,N*-diglycidylaniline. As a result we found that the fractional DSE equation is also obeyed for pressure pathways.

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## I. INTRODUCTION

Dielectric spectroscopy is a method that allows an observation of two kinds of motion in a liquid. They are monitored simultaneously and irrespectively of each other. The first of these refers to a transport process of free ionic species which are present in almost every liquid. This migration of charged carriers in the presence of an electric field is known as dc conductivity. The second type of molecular motion probed by dielectric spectroscopy deals with the orientational relaxation of dipolar molecules. Although these motions concern different sorts of particles, they are not generally independent. Very recently, Stickel *et al.* [1] pointed out that a variation of dc conductivity  $\sigma$  with temperature in some glass forming liquids is similar to the temperature dependence of the orientational relaxation time  $\tau$ .

Based on hydrodynamic approaches [2], one can derive a simple relationship between  $\sigma$  and  $\tau$  [1]. This result is known as the Debye-Stockes-Einstein (DSE) relation:

$$\sigma\tau \cong \text{const.} \quad (1)$$

As the dielectric spectroscopy is able to cover an extraordinary range of changes of both  $\sigma$  and  $\tau$ , this method turns out to be one of the most appropriate to check the validity of the upper relation. The DSE model was widely verified in liquids with low viscosity, and the coupling between conductivity and rotational relaxation time became obvious [1,3–5]. On the other hand, the breakdown of the DSE law was found in many systems with high viscosity on approaching the glass transition [6–9]. In this case, the relationship between the conductivity and rotational relaxation time can be well described by means of a fractional Debye-Stokes-Einstein (FDSE) law,

$$\sigma\tau^s \cong \text{const.} \quad (2)$$

where  $s$  is a fractional exponent less than 1.

The decoupling of the reorientation and translation was thoroughly discussed in recent review articles by Sillescu [10] and Ediger [11]. The decoupling between rotational and translational motions appears not only as a fact traced experimentally on a temperature path by NMR and optical meth-

ods; theoretical concepts are also given in which this problem is combined with the heterogeneity of supercooled systems. In one study translational and rotational motions were shown to be dependent on subsystems of fast or slow molecules, respectively. This is why detecting different  $T$  dependences of  $D_{trans}$  and  $D_{rot}$  may provide evidence of the existence of these two subensembles, as well as the existence of heterogeneity in the whole system.

The relations quoted above were mainly tested in temperature variable experiments. However, it is a well known fact that both  $\sigma$  and  $\tau$  can also be controlled by pressure changes [12]. Therefore, the important question is whether the DSE and FDSE models are also valid for a pressure pathway. At the present time, practically, there are no experimental results with regard to the relationship between  $\sigma$  and  $\tau$  under conditions of high compression. The use of pressure as an additional thermodynamical variable in studying the coupling between  $\sigma$  and  $\tau$  provoked another question: whether the fractional exponent in Eq. (2), determined from isothermal and isobaric measurements, has the same value. These questions were the chief motivation for this work. The results obtained in liquids tested by us are very promising, and inclined us toward further work on that problem.

## II. EXPERIMENT

As a material for the test we chose two very similar low molecular liquids, *N,N*-diglycidyl-4-glycidyoxyaniline (DGGOA) and *N,N*-diglycidylaniline (DGA), with structural formulas presented in Fig. 1. Both samples were purchased from Aldrich Chemicals. The compounds turn out to be perfect for our research for some reasons: (i) they have no ten-

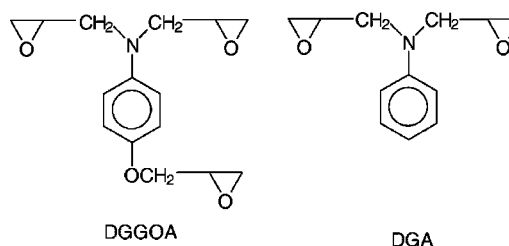


FIG. 1. The structural formula of the studied molecules.

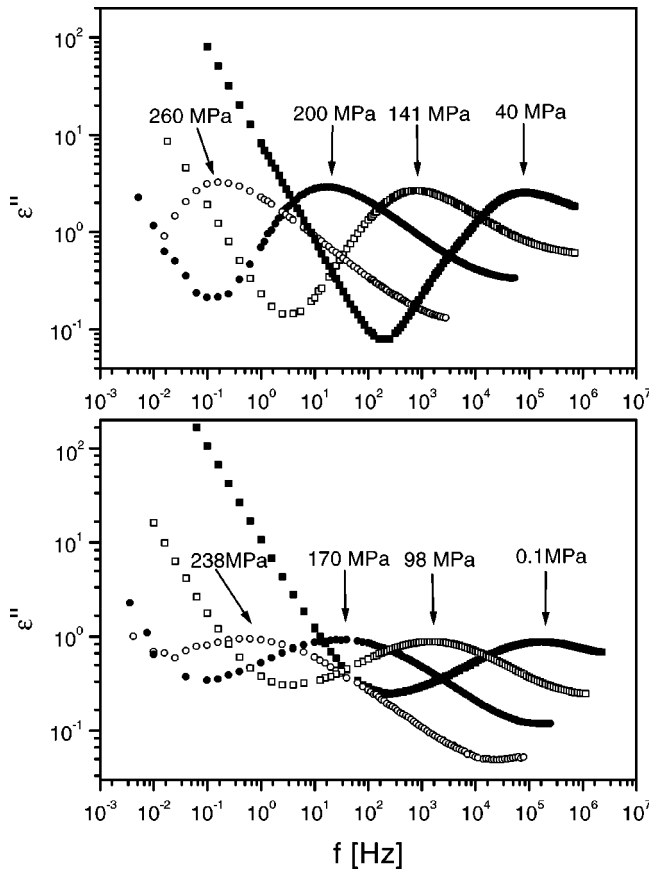


FIG. 2. Dielectric loss spectra of DGGOA (upper graph) and DGA (lower graph) obtained in labeled pressures.

dency toward crystallization; (ii) they exhibit a permanent dipole moment originating from epoxy groups; (iii) they reveal a conductivity due to the ionic impurities; and (iv) in the case of both samples, there is no need to use very low temperatures for experiments.

The complex dielectric permittivity  $\varepsilon^* = \varepsilon' + i\varepsilon''$  was measured in the frequency range from  $10^{-2}$  up to  $10^7$  Hz by applying two different measurement systems: a frequency response analyzer (Solartron SI-1260) and an impedance analyzer (HP-4192A). The pressure was measured by a Nova Swiss tensometric pressure meter, with a resolution of  $\pm 0.1$  MPa. The temperature was controlled within  $\pm 0.1$  K by means of a liquid flow provided by a thermostatic bath. More details about the experimental setup can be found in Ref. [13].

The temperature measurements (under atmospheric pressure) were provided in the ranges 270–300 K for DGGOA and 203–293 K for DGA. The pressure experiments (for isotherm at  $T=263$  K) were carried out in the ranges 0.1–260 MPa for DGGOA and 0.1–238 MPa for DGA.

### III. RESULTS AND DISCUSSION

Figure 2 is a representative example of experimentally obtained dielectric loss data  $\varepsilon''(f)$  for both measured samples under high pressure. Both DGA and DGGOA reveal two common types of relaxation, i.e., the  $\alpha$  relaxation, with an origin in the reorientation of terminal polar groups (epoxy

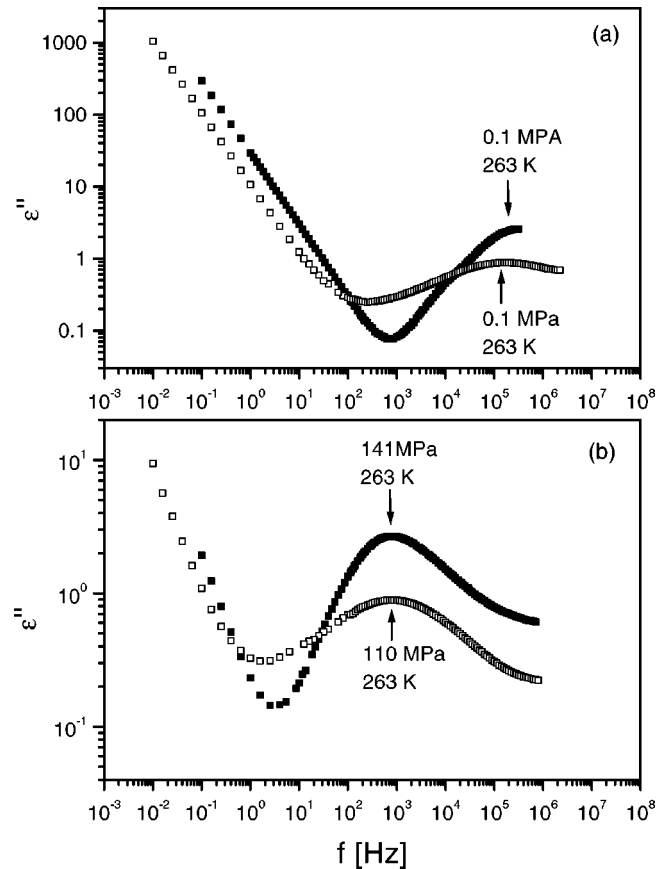


FIG. 3. Comparison of the shape of the imaginary parts of the dielectric permittivity of DGGOA (solid square) and DGA (open square). (a) For the same thermodynamical conditions. (b) For the same relaxation times (the maximum of the loss curve falls on the same frequency). The meaning of the symbols is the same as in the upper graph.

groups), and dc conductivity relaxation associated with the translation of small ions. The ionic signal is thought to be due to sodium and chloride ions. In some amounts these are almost always present in chemicals. In particular, dipolar liquids, stored in air atmosphere are expected to absorb such impurities. The  $\alpha$ -relaxation process is related to the glass transition [5]. Additionally, in both compounds one extra relaxation appears, named  $\alpha'$ , which has an intensity much lower in comparison to the  $\alpha$  process. This relaxation is visible only at moderate temperatures and pressures, and disappears when the sample approaches the glass transition. The presence of the  $\alpha'$  peak in dielectric loss spectra of DGGOA was recently indicated by Corezzi *et al.* However, there is no final conclusion about its nature. In the case of DGA the  $\alpha'$ -relaxation process is additionally covered by dc conductivity, and can be clearly observed only in the real part of the dielectric permittivity.

Figure 3 presents a comparison of the dielectric loss curves of both studied compounds. In the upper graph one can see spectra measured under the same thermodynamical conditions, whereas the lower graph shows a comparison of curves with the same relaxation times. From Fig. 3 it is evident that the same relaxation time for DGA can be reached under slightly milder conditions than for DGGOA, and the

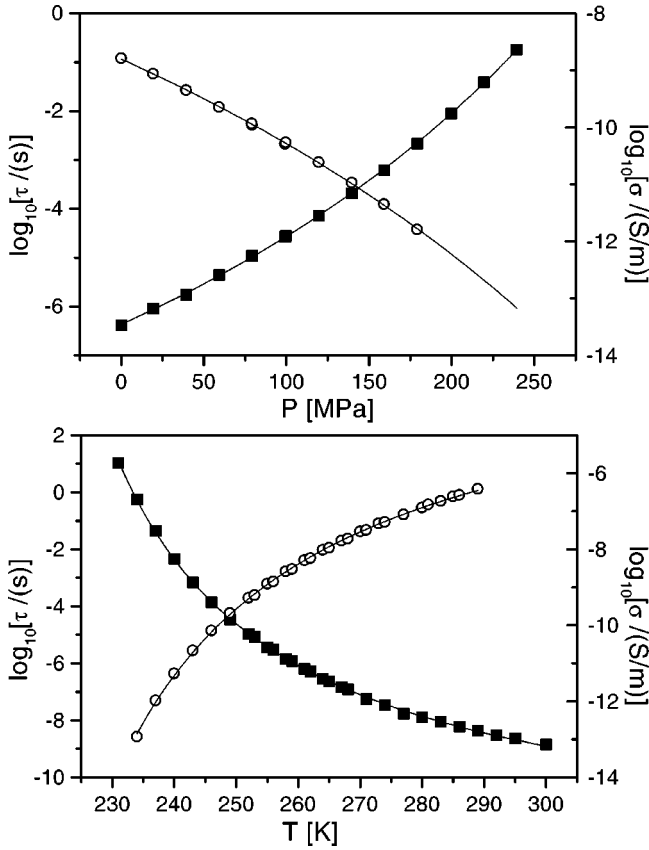


FIG. 4. Logarithm of the dc conductivity (open circle) and  $\alpha$  relaxation time (solid square) of DGGOA vs temperature (upper) and pressure (lower). Solid lines indicate fits to the VFT law (in a proper form).

relaxation strength of the former compound is smaller than of the latter.

In order to determine both the relaxation times  $\tau$  and conductivity  $\sigma$  from the dielectric permittivity curve the data, were analyzed by means of the Havriliak-Negami (HN) function with a conductivity term  $\sigma/\omega\epsilon_0$ . In cases where two relaxation processes are visible, a second Havriliak-Negami function [14] was added. Therefore, the most complex fit function had the form

$$\begin{aligned} \epsilon^* = & i \frac{\sigma}{\omega\epsilon_0} + \epsilon_\infty + (\epsilon_s - \epsilon_1) [1 + (i\omega\tau_1)^{\alpha_1}]^{\gamma_1} \\ & + (\epsilon_s - \epsilon_1) [1 + (i\omega\tau_2)^{\alpha_2}]^{\gamma_2}, \end{aligned} \quad (3)$$

where  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_\infty$  denotes the asymptotic value of the permittivity at high frequency,  $\epsilon_s$  is the permittivity at the other limit, and the subscripts 1 and 2 refer to the  $\alpha$  and  $\alpha'$  processes, respectively. The relaxation times were calculated as  $1/2\pi f_{\max}$ , where  $f_{\max}$  denotes the frequency of the maximum of the dielectric loss. The results obtained from the HN analysis are collected in Figs. 4 and 5. Vogel-Fulcher-Tammann (VFT)-type equations have been used to analyze the relaxation data. From the fitting procedure we found that the pressure and temperature depen-

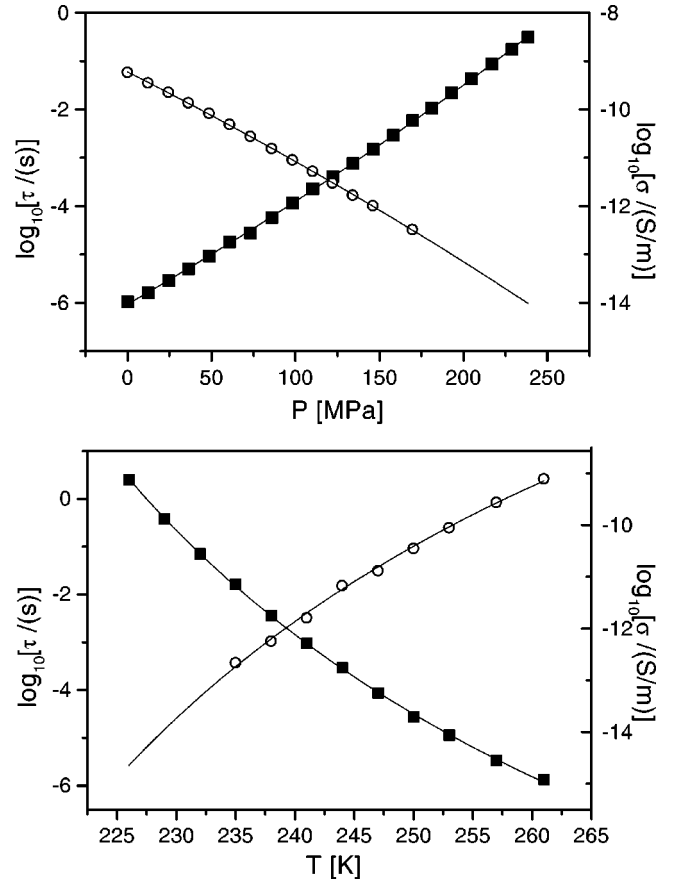


FIG. 5. Logarithm of the dc conductivity (open circle) and  $\alpha$  relaxation time (solid square) of DGA vs temperature (upper graph) and pressure (lower graph). Solid lines indicate fits to the temperature and pressure VFT laws, respectively.

dences of the relaxation times are well described by the VFT function in its temperature [Eq. (4)] [15] and pressure [Eq. (5)] [16] forms, respectively:

$$\tau = \tau_0 \exp\left(\frac{D_T T_0}{T - T_0}\right), \quad (4)$$

$$\tau = \tau_{0P} \exp\left(\frac{D_P P}{P_0 - P}\right). \quad (5)$$

Here  $\tau_0$  is a characteristic time constant of the order of magnitude  $10^{-13}$ ,  $\tau_{0P}$  is a relaxation time in the atmospheric pressure,  $T_0$  and  $P_0$  are the temperature and pressure of an ideal glass, and  $D_T$  and  $D_P$  are dimensionless parameters called strength parameters. It also turns out that the temperatures and pressure behaviors of the conductivity may be well reproduced by a VFT-like function, where  $\tau$  is replaced by  $\sigma$  and  $\tau_0$  is replaced by  $\sigma_0$ . The analysis of relaxation times by means of the temperature VFT equation showed that DGGOA is a more fragile glass former ( $D_T=4.4$ ) than DGA ( $D_T=14.3$ ), which could be classified as a middlingly strong glass ( $D_T>10$ ).

Now we return to our main problem concerning the relation between  $\sigma$  and  $\tau$ . If the FDSE equation is a suitable description of the relation between these two quantities one can observe, on a log-log scale, a linear dependence with the

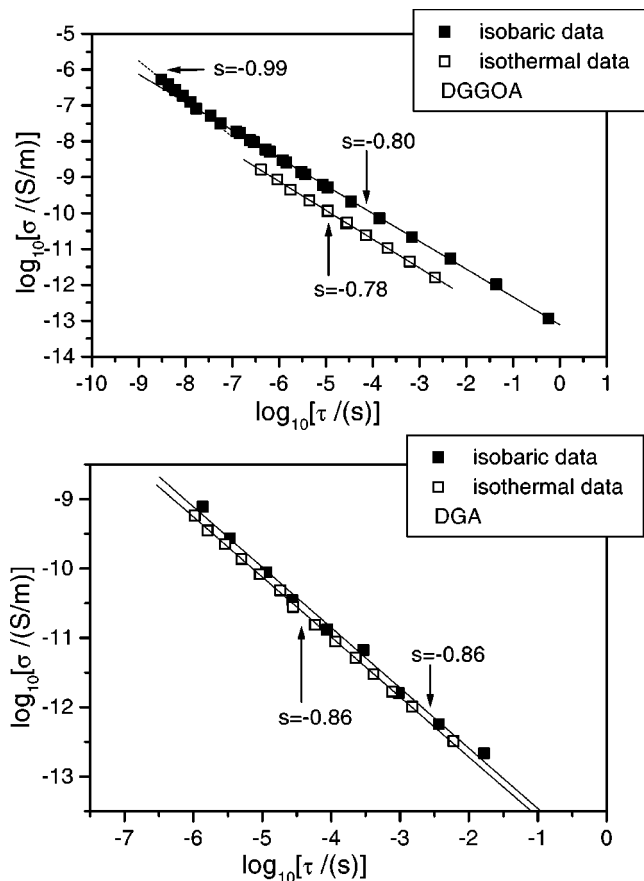


FIG. 6. dc conductivity vs relaxation times on a log-log scale obtained for isothermal (solid square) and isobaric (open square) data. The upper graph presents data obtained for DGGOA, and the lower graph that obtained for DGA. The solid lines represent fits to the FDSE equation. On the upper graph, the dashed line corresponds to the DSE law.

slope corresponding to the exponent  $s$ . The results in Fig. 6 prove that for temperature data the FDSE law is a good description for both compounds. It is worth noting that the value of the fractional exponent which we determine for DGGOA is close to the one reported by Corezzi *et al.* In the upper graph a region is also visible where the DSE relation is fulfilled ( $s=0.99$ ). This is a region of rather high tempera-

tures (292–271 K), corresponding to an ordinary liquid for which reorientational and translational motions are still coupled.

More general conclusions result from an analysis of the isothermal data. In Fig. 6 we plot  $\log \sigma$  versus  $\log \tau$  for isothermal measurements (open symbols).

First, it turns out that the FDSE equation also well describes data obtained for pressure pathways. The isothermal and isobaric data for DGGOA do not collapse onto the same straight line, as some drift in the absolute magnitude of the conductivity occurs over a period of months (isobaric and isothermal experiments are carried out year after year). A slight shift between pressure and temperature data, which were obtained at the same time, is also observed for DGA. This results from the fact that we used different capacitors and measurement systems for isothermal and isobaric experiments.

Second, the slopes  $s$  from studies of both kinds of samples are the same. This means that although changes of pressure and temperature induce changes of different properties (temperature mainly influences the activation energy, and pressure leads to changes in the intermolecular distances), the way of carrying out experiments is not important for the relation between  $\sigma$  and  $\tau$ . These results imply that the fractional exponent  $s$  could be considered an important parameter characterizing a given liquid.

#### IV. CONCLUSIONS

Summing up our work, we can state that in a supercooled region the fractional Debye-Stokes-Einstein equation provides a good description of the relationship between translational and rotational motions in liquid. On the other hand, the Debye-Stokes-Einstein equation is only valid for ordinary liquids with low viscosity. We have also proved that the fractional exponent  $s$  has the same value regardless of whether the experiments were carried out under conditions of constant pressure or constant temperature.

#### ACKNOWLEDGMENT

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