

High-pressure and temperature dependence of dielectric relaxation in supercooled di-isobutyl phthalate

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Results are presented for isothermal, high-pressure (up to $p=300$ MPa), and temperature (under atmospheric pressure) measurements of complex dielectric permittivity in supercooled di-isobutyl phthalate. The relaxation times determined from the temperature study obey the temperature Vogel-Fulcher-Tammann (VFT) law. The pressure dependence of relaxation times describes the relation $\tau=\tau_0\exp[B/(p-p_0)]$. This equation gives the same ideal glass transition pressure p_0 as the generalized VFT formula proposed by Leyser *et al.* [Phys. Rev. E **51**, 5899 (1995)]. For isobaric and isothermal absorption curves, the scaling behavior has been also tested. [S1063-651X(96)08710-7]

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INTRODUCTION

One of the basic problems concerned with “relaxation properties” of supercooled liquids is finding universal descriptions for the whole glass family. There are many empirical forms proposed which describe the behavior as the glass transition is approached. Attempts of scaling in the dielectric relaxation have been made [1]. The most commonly used thermodynamical parameter which induces the glass transition is the temperature. For many liquids the relaxation time in the vicinity of the glass transition temperature depends on temperature according to the empirical Vogel-Fulcher-Tammann (VFT) law [2]. There are very few papers concerning experimental studies of high-pressure (p) influence on the relaxation behavior in supercooled liquids [3,4]. Basing on pressure and temperature measurements of viscosity in glycerine and di-butyl phthalate, Cook *et al.* [5] found that the VFT relation is also valid also for high-pressure isobars. Leyser *et al.* [6] studied the pressure behavior of relaxation times in *o*-therphenyl using specific-heat spectroscopy. These data have been compared with the extended Vogel-Fulcher-Tammann law [6,7]

$$\tau = \tau_0 \exp\left(\frac{B - b(p - 0.1 \text{ MPa})}{T - [T_0 + a(p - 0.1 \text{ MPa})]}\right), \quad (1)$$

where a , b , and B are constants, and T_0 is the so-called ideal glass transition temperature.

In this paper results of isothermal, high-pressure (up to 300 MPa) measurements of complex dielectric permittivity in supercooled di-isobutyl phthalate are presented. For comparison, the temperature behavior (under atmospheric pressure) was also tested. Our chief motivation was to find one pressure-parameter formula which describes isothermal measurements of relaxation times dependent on pressure. We have analyzed our results by taking into account the possibility of replacing the temperature with pressure in the VFT description. The pressure and temperature absorption curves are also compared by applying simple scaling.

EXPERIMENT

Di-isobutyl phthalate obtained from Polskie Odczynniki Chemiczne (POCH, Poland) has been purified by distillation procedures. Di-isobutyl phthalate as a medium fragile, low molecular liquid, was selected because this system has several advantages: first of all it does not crystallize, and low temperatures are not required in order to examine dielectric relaxation as a pressure function in the frequency range which we are interested in. For different temperatures and pressures we obtained the complex dielectric function $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ in the frequency range 10^{-2} – 10^7 Hz. In this frequency range we used two systems: a frequency response analyzer (Solartron SI-1260) and an impedance analyzer (HP-4192 A). For temperature studies under atmospheric pressure, the sample temperature has been controlled by a temperature controller (Unipan 660) using a N_2 stream. The temperature stability of the sample is better than 0.1 K measured over the period of the frequency sweep.

Pressure measurements were performed on an apparatus made by High Pressure Research Center Unipress (Warsaw, Poland). The capacitor, filled with tested liquid, was placed in the high-pressure chamber. Pressure was exerted on the chamber from a pressure source (special chamber with a piston placed under hydraulic press) through a mixture of heptane and silicone oil. The capacitor which was constructed in our laboratory was made from a stainless steel. The tested sample was in contact only with the stainless steel, teflon, and quartz. The pressure was measured by a Nova Swiss tensometric pressure meter with a resolution ± 0.1 MPa. The pressure chamber was thermostated with an accuracy better than 0.1 K. The temperature was measured by means of a Keithely 195A with a platinum resistor (class A1, DIN 43 760) which was located in the jacket of the chamber and a copper-constantan thermocouple placed inside the pressure chamber. Detailed description of the pressure apparatus and the pressure capacitor are given elsewhere [8].

RESULTS AND DISCUSSION

Pressure measurements of the complex dielectric permittivity (ε^*) were performed for two isotherms ($T_1=238$ K and $T_2=248.5$ K). Figure 1 shows the normalized imaginary part

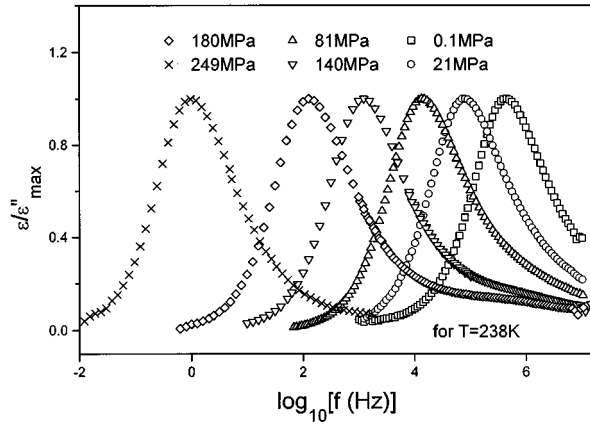


FIG. 1. Imaginary part ε'' of ε vs $\log_{10}[f(\text{Hz})]$ at labeled pressure.

of the dielectric susceptibility $\varepsilon''/\varepsilon''_{\max}$ for di-isobutyl phthalate over the available frequency range for the isotherm $T_1=238$ K. Each absorption curve corresponds to a different pressure. The observed α -relaxation peaks in ε'' show increasing relaxation times τ with increasing pressure, similar to the divergence of τ when the glass temperature is approached by lowering the temperature at constant pressure. The pressure dependence of relaxation times for both tested isotherms are shown in Fig. 2. The data can be fitted by an equation (solid line)

$$\tau = \tau_0 \exp[B/(p_0 - p)], \quad T = \text{const}, \quad (2)$$

where B and τ_0 are constants, and p_0 in analogy to T_0 is a pressure of an ideal glass transition. The obtained values of parameters are given in Table I.

Formula (2) has a functional form isomorphic to VFT equation described by Eq. (3),

$$\tau = \tau_0 \exp[A/(T - T_0)], \quad p = 0.1 \text{ MPa}, \quad (3)$$

where A is a constant, and T_0 is so-called ideal glass transition temperature. The VFT relation was introduced to ana-

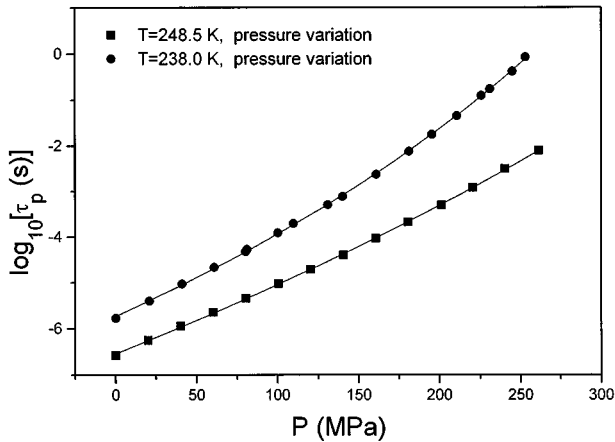


FIG. 2. Logarithm of time relaxation vs pressure at two fixed temperatures $T=248.5$ K (filled squares) and $T=238$ K (filled circles). The solid lines are fits according to $\tau = \tau_0 \exp[B/(p_0 - p)]$ equation.

TABLE I. Fitting parameters for the data in Figs. 2 and 3 using the $\tau = \tau_0 \exp[B/(p_0 - p)]$ equation and the Vogel-Fulcher-Tammann form, respectively.

Variable	T_0 (K)	p_0 (MPa)	A, B (K, MPa)	$\ln[\tau_0(s)]$
T ($p = \text{atm.}$)	151 ± 1	atm.	1469 ± 20	-30.1 ± 0.2
p ($T = 248.5$ K)	248.5 ± 0.1	1461 ± 10^2	69000 ± 10^3	-62 ± 4
p ($T = 238$ K)	238 ± 0.1	893 ± 30	29000 ± 2300	-46 ± 1.5

lyze the temperature dependence of τ in glass-forming materials. It is also valid for relaxation times in di-isobutyl phthalate (Fig. 3) which were studied here [9]. Fitting parameters are given in Table I.

The equivalence of temperature and pressure (field variables) is a well-known fact in continuous phase transition studies (isomorphism critical phenomena [10]). Formula (2) can be also derived by using Doolite equation written in a form

$$\tau = \tau_0 \exp(B'/V_f), \quad (4)$$

where V_f is a free volume.

Substituting this equation with $V_f \approx \kappa(p - p_0)$ ($T = \text{const}$, and κ is an isothermal compressibility coefficient), relation (2) is obtained. Introducing $V_f = \alpha(T - T_0)$ ($p = \text{const}$, and α denotes the thermal expansion coefficient) one can obtain the VFT relation (3) [11].

Relaxation times obtained from the isothermal measurements can be also described by Eq. (1). Next from Eq. (1) we can obtain the pressure p_0 . For the isothermal data presented in this paper, using formula (1), a set of glass transition pressure data was obtained: for $T=248.5$ K, $p_0=1461$ MPa, and for $T=238$ K, $p_0=895$ MPa. Formulas (1) and (2) lead to the same pressure value p_0 for given temperatures. One should notice that Eq. (2) needs lower fitting parameters than the generalized Vogel-Fulcher-Tammann law (1).

Figure 4 shows the simple scaling of obtained absorption curves for chosen isotherms and isobars in a double log-log scale. It is visible that the left, low-frequency, wings for all curves follow the same relation:

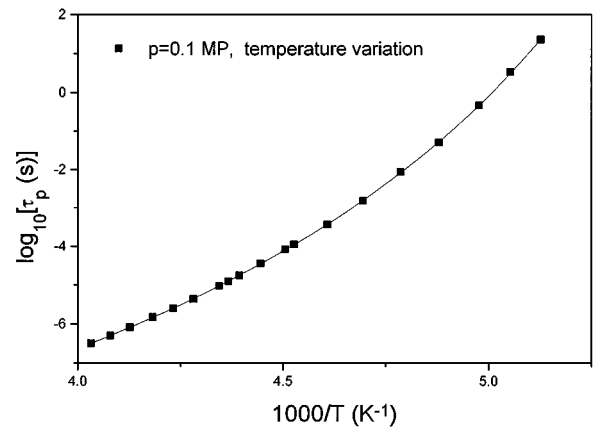


FIG. 3. Logarithm of time relaxation $\log_{10}[\tau(s)]$ vs $1000/T$ (K^{-1}). The curve is a fit to the dielectric data using the Vogel-Fulcher-Tammann form; the data points that were fitted are designated by solid squares.

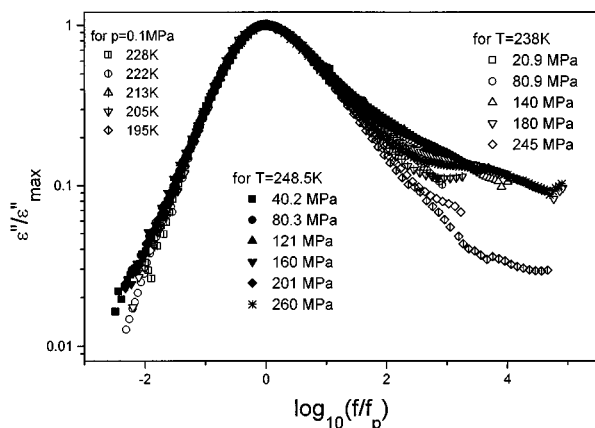


FIG. 4. Masterplot for the α -relaxation of di-isobutyl phthalate: $\varepsilon''/\varepsilon''_{\max}$ vs f/f_{\max} (ε''_{\max} describes the maximum value of ε'' at the frequency f_{\max}).

$$\frac{\varepsilon''}{\varepsilon''_{\max}} \propto \left(\frac{f}{f_p}\right)^m \quad \text{with } m \approx 1 \text{ and } f < f_p. \quad (5)$$

The high-frequency wing ($f > f_p$) is strongly influenced by the second relaxation process, particularly for higher pressures and lower temperatures. An attempt to analyze these curves by a superposition of two Havriliak-Negami functions [12] is shown in Fig. 5.

As a conclusion, we have shown in this paper that pressure and temperature may be treated as equivalent, isomorphic, thermodynamic variables in a supercooled liquid. The influence of pressure and temperature on the free volume in the vitrification process was previously analyzed by means of computer simulation in Lennard-Jones systems [13]. It was stated that the volume in which the glass transition oc-

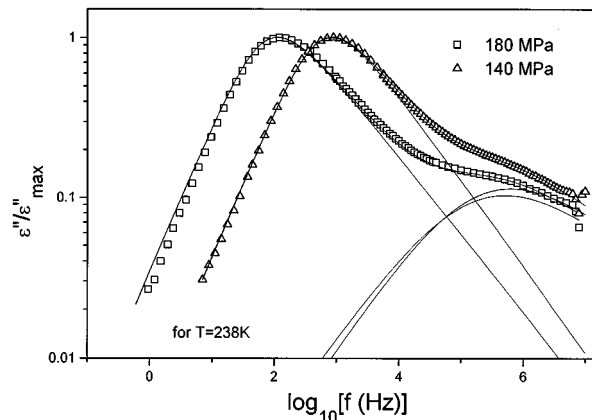


FIG. 5. Formal fit to describe the high-frequency wing by superposition of two HN-relaxation processes. The fit parameters for the measurement at 180 MPa are as follows: First process: $\Delta\varepsilon=4.59$, $\alpha=0.93$, $\beta=0.52$, and $\tau=3.33 \times 10^{-3}$ s; Second process: $\Delta\varepsilon=0.87$, $\alpha=0.55$, $\beta=0.54$, and $\tau=1.12 \times 10^{-6}$ s. At 140 MPa the measurements are as follows: First process: $\Delta\varepsilon=4.34$, $\alpha=0.93$, $\beta=0.58$, and $\tau=3.07 \times 10^{-4}$ s. Second process: $\Delta\varepsilon=0.9$, $\alpha=0.57$, $\beta=0.51$, and $\tau=7.77 \times 10^{-7}$ s.

curs is the same when the temperature or pressure is changed. Results obtained in this paper seem to confirm the idea that the same value of the free volume is reached independently if pressure or temperature is changed.

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