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 \( \tau = \tau_0 \exp\left[\frac{B - b(p - p_0)}{T - \left(T_0 + a(p - p_0)\right)}\right] \),

\[ \tau = \tau_0 \exp\left(\frac{B - b(p - p_0)}{T - \left(T_0 + a(p - p_0)\right)}\right), \tag{1} \]

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.

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 for high-pressure isobars. Leyser et al. [6] studied the pressure behavior of relaxation times in \( o \)-terphenyl using specific-heat spectroscopy. These data have been compared with the extended Vogel-Fulcher-Tammann law [6,7]

\[ \tau = \tau_0 \exp\left(\frac{B - b(p - p_0)}{T - \left(T_0 + a(p - p_0)\right)}\right), \]

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

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 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 \( \pm 0.1 \) 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 \( \varepsilon^* \) were performed for two isotherms \( (T_1=238 \) K and \( T_2=248.5 \) K). Figure 1 shows the normalized imaginary part...
TABLE I. Fitting parameters for the data in Figs. 2 and 3 using the \( \tau = \tau_0 \exp \left[ B/(p_0 - p) \right] \) equation and the Vogel-Fulcher-Tammann form, respectively.

<table>
<thead>
<tr>
<th>Variable</th>
<th>( T_0 ) (K)</th>
<th>( p_0 ) (MPa)</th>
<th>( A, B ) (K, MPa)</th>
<th>( \ln[\tau_0(s)] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) (p=atm.)</td>
<td>151 ±1 atm.</td>
<td>1469 ±20</td>
<td>-30.1 ±0.2</td>
<td></td>
</tr>
<tr>
<td>( p ) (( T=248.5 ) K)</td>
<td>248.5 ±0.1</td>
<td>1461 ±10(^2)</td>
<td>69000 ±10(^3)</td>
<td>-62 ±4</td>
</tr>
<tr>
<td>( p ) (( T=238 ) K)</td>
<td>238 ±0.1</td>
<td>893 ±30</td>
<td>29000 ±2300</td>
<td>-46 ±1.5</td>
</tr>
</tbody>
</table>

lyze the temperature dependence of \( \tau \) 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

\[
\tau = \tau_0 \exp \left( B'/(V_f) \right),
\]

where \( V_f \) is a free volume.

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

Relaxation times obtained from the isothermal measurements can also be 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:

\[
1/T \approx \alpha \log_{10} \sigma(p).
\]
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 occurs 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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