

The influence of pressure on dielectric relaxation for phthalate derivatives in the supercooled state

M Paluch, J Ziolo, S J Rzoska and P Haldas

Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

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Abstract. The dielectric relaxation of phthalate derivatives in the supercooled state has been studied at pressures up to 300 MPa, covering a frequency range from 10^{-1} to 10^7 Hz. The behaviour of the relaxation time τ is very well reproduced by the relation $\tau = \tau_0 \exp(Bp/(p_0 - p))$. The analysis of the absorption curves shows that pressure increases the amplitude of the β -relaxation more than the equivalent temperature change. The scaling form presented by Dixon and co-workers for the α -process in supercooled liquids is re-examined in the light of pressure–dielectric relaxation data. It was found that Dixon scaling distinguishes isothermal measurements from isobaric measurements, by means of the greater strength of the second relaxation process (β) for the pressure path.

1. Introduction

During recent years, a great deal of effort has gone into the study of the dynamics of α -relaxation in supercooled liquids. It has been established that the α -relaxation shows some universal features, irrespective of the type of glass-forming system considered. The rapid increase of the viscosity or characteristic relaxation time τ with decreasing temperature, and the non-Debye behaviour of the relaxation function are among the most important features of the relaxation process. The temperature dependence of the relaxation times is usually analysed by means of the Arrhenius relation and the Vogel–Fulcher equation [1], although the range of application of these relations is still a very controversial topic [2–5].

Recently, Dixon *et al* [6] reported a scaling form for primary (α -) relaxation that collapsed absorption peaks onto a single scaling curve by plotting $w^{-1} \log_{10}(\epsilon'' f_p / \Delta \epsilon f)$ versus $w^{-1}(w^{-1} + 1) \log_{10}(f/f_p)$ for low-molecular-weight glass-forming liquids over a wide frequency range. However, some authors claim that no master curve can be obtained for glass-forming systems [7–10].

Up to now, the thermodynamical parameter most often used to investigate the relaxation processes has been temperature; pressure is very rarely used for this purpose. Thus the question arises of whether there are any differences between the dynamics of the system when the glass transition is approached via temperature changes and the dynamics when it is approached via isothermal density changes. Pressure studies can also provide important information about the molecular relaxation mechanisms.

A great number of theoretical models have been used to analyse the temperature dependence of the relaxation times [11–16]. For the pressure dependence, data are typically compared with the free-volume model [17–20].

There are several experimental papers available which analyse the influence of pressure on the shape of the loss peaks obtained from dielectric studies [21–24]. In particular, the

scaling formula proposed by Dixon has not been tested yet for absorption curves obtained from pressure measurements.

The aim of our studies was to examine the problems mentioned above. We have also demonstrated the influence of pressure on β -relaxation. Moreover, the applicability of the Dixon scaling for different pressures and different materials was tested. Some further conclusions arose from a comparison of the results for phthalate derivatives and their mixtures.

2. Experiment

Measurements were conducted on the following glass-forming liquids: bis(2-ethylhexyl) phthalate, diethyl phthalate, dibutyl phthalate, dipentyl phthalate, diallyl phthalate, diisonyl phthalate, (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19}, (dimethyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5}, and (dibutyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5}, where the subscripts denote the concentrations given as mole fractions, over a wide pressure range (up to 300 MPa). For comparison, data for di-isobutyl phthalate, taken from [21], are also presented.

Except the pentyl phthalate (POCH), all of our samples were purchased from FLUKA, and they were purified by distillation at reduced pressure. The samples tested—except the dimethyl phthalate, which showed a strong tendency towards crystallization—can easily be supercooled over a wide range of pressures and temperatures.

The dielectric measurement covered the frequency range from 10^{-1} to 10^7 Hz. Two different measurement systems were used: a frequency response analyser (Solartron SI-1260), and a Hewlett–Packard impedance analyser (4192A).

Measurements were performed using a pressure system with a specially designed measurement capacitor, described in detail elsewhere [25]. This enabled the sample tested to be totally isolated from the medium delivering the pressure (a mixture of hexane and silicone oil): the sample was in contact only with stainless steel, Teflon, and quartz. The pressure chamber was thermostated to an accuracy of better than 0.1 K. The temperature was measured by means of a Keithley 195 A multimeter with a platinum resistor (A1 class, DIN 43 760, resolution ± 0.01 K) located in the jacket of the chamber. Additionally, a copper–constantan thermocouple was placed inside the chamber. The pressure was measured by a Nova Swiss tensometric pressure meter with a resolution of 0.1 MPa.

The relaxation times have been determined from the position of the ϵ'' -peaks, and their values for the pure components are collected together in table 1. The numerical analysis of the data was performed by means of the ORIGIN 3.5 software (Microcal Incorporated).

3. Results and discussion

An example of the measured dielectric function $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$ for bis(2-ethylhexyl) phthalate, for different pressures and a constant temperature of $T = 239.7$ K, is presented in figure 1. The behaviour obtained and the quality of data are typical for all of the materials tested. The absorption curves move towards lower frequencies while the pressure is increased. The reciprocal of the frequency of the absorption peak is taken as a measure of the characteristic relaxation time. The relation most commonly applied for the description of the evolution of relaxation times with pressure is the pressure analogue of the Arrhenius

Table 1. Relaxation time data for the pure components from isothermal experiments.

Di-isobutyl phthalate				Bis(2-ethylhexyl) phthalate			
$T = 238 \text{ K}$		$T = 248.5 \text{ K}$		$T = 252.8 \text{ K}$		$T = 239.7 \text{ K}$	
p (MPa)	$\log_{10}[\tau \text{ (s)}]$	p (MPa)	$\log_{10}[\tau \text{ (s)}]$	p (MPa)	$\log_{10}[\tau \text{ (s)}]$	p (MPa)	$\log_{10}[\tau \text{ (s)}]$
0.1	-5.767	0.1	-6.575	170	-4.382	282.3	-1.381
20.9	-5.398	20.2	-6.251	151.1	-4.594	260.3	-1.681
40.9	-5.023	40.2	-5.939	131	-4.810	240.3	-2.009
60.8	-4.659	60.1	-5.641	110	-5.038	221.7	-2.321
80.1	-4.318	80.3	-5.338	90.2	-5.242	200.9	-2.639
80.9	-4.272	100.7	-5.021	70.2	-5.453	181.7	-2.933
100.1	-3.905	120.3	-4.710	50.1	-5.672	161.8	-3.224
109.9	-3.703	140.6	-4.393	30.1	-5.886	140.2	-3.525
130.9	-3.29	160.5	-4.03	15.6	-6.048	120.5	-3.800
140	-3.109	180.8	-3.67	0.5	-6.232	100.5	-4.077
160.8	-2.624	201.4	-3.3	261.4	-3.309	80.5	-4.348
181.2	-2.12	220.4	-2.91	241.3	-3.550	60.5	-4.606
195.5	-1.743	240.3	-2.5	220.7	-3.788	46.2	-4.802
210.6	-1.337	261.4	-2.1	201.4	-4.011	29.7	-5.027
225.7	-0.895			180.8	-4.242	13	-5.237
231	-0.753			161.8	-4.455	0.5	-5.426
244.8	-0.373			140.3	-4.683		
253	-0.065			120.7	-4.897		
				91.5	-5.217		
				50	-5.677		

Dibutyl phthalate		Pentyl phthalate		Di-isonyl phthalate		Diethyl phthalate		Diallyl phthalate	
$T = 243 \text{ K}$		$T = 247.2 \text{ K}$		$T = 248.9 \text{ K}$		$T = 248.6 \text{ K}$		$T = 248.2 \text{ K}$	
p (MPa)	$\log_{10}[\tau \text{ (s)}]$	p (MPa)	$\log_{10}[\tau \text{ (s)}]$	p (MPa)	$\log_{10}[\tau \text{ (s)}]$	p (MPa)	$\log_{10}[\tau \text{ (s)}]$	p (MPa)	$\log_{10}[\tau \text{ (s)}]$
242	-4.737	261.7	-4.686	261.5	-3.239	289.1	-3.636	241.1	-5.366
221.4	-4.951	240.9	-4.888	240.5	-3.495	272.8	-3.910	229.3	-5.610
201.3	-5.153	221	-5.076	220.1	-3.712	251.1	-4.275	209.8	-5.826
181.4	-5.348	201	-5.261	199.7	-3.949	229.8	-4.622	189.9	-6.033
160	-5.561	181.6	-5.434	181.1	-4.158	209.8	-4.947	169.7	-6.2421
141.4	-5.745	160.8	-5.617	160.6	-4.392	189.6	-5.252	149.8	-6.455
120.3	-5.937	140.9	-5.796	140.4	-4.614	170.9	-5.540	129.6	-6.674
100.4	-6.118	120.7	-5.972	120.2	-4.842	149.9	-5.861	129.6	-6.685
82.1	-6.289	100.7	-6.145	99.6	-5.072	129.8	-6.150		
59.9	-6.486	80.5	-6.325	80	-5.291	109.8	-6.454		
40.7	-6.651	59.7	-6.514	60.8	-5.514	91.4	-6.761		
20.5	-6.844	39.7	-6.715	39.7	-5.745				
		20.6	-6.908	19.1	-5.982				
				0.7	-6.196				

relation [24]:

$$\tau = \tau_0 \exp\left(\frac{pV^*}{RT}\right) \quad (1)$$

where V^* is the activation volume.

The applicability of relation (2) was demonstrated on the basis of dielectric measure-

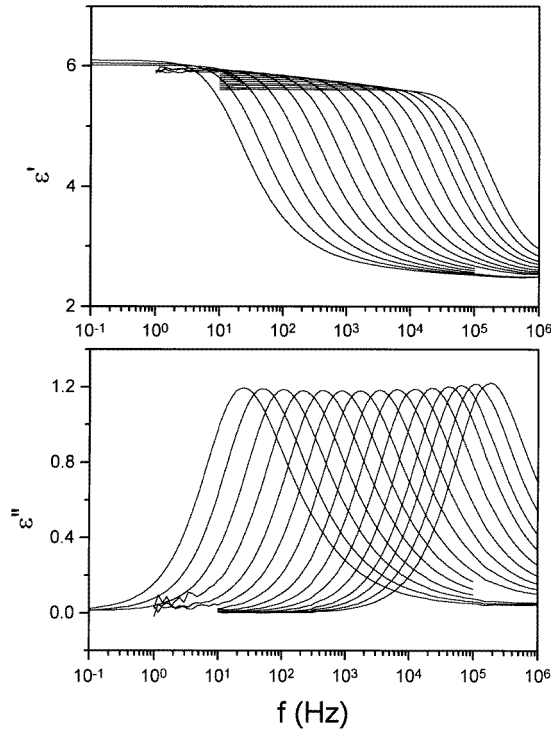


Figure 1. The real and imaginary parts, ε' and ε'' , of the dielectric susceptibility of bis(2-ethylhexyl) phthalate versus frequency at constant temperature, $T = 239.7$ K and different pressures. The solid lines represent experimental data. The frequency of the absorption peak decreases with increasing pressure.

ments for di-isobutyl phthalate [21]:

$$\tau = \tau_0 \exp\left(\frac{A}{p_0 - p}\right) \quad (2)$$

where p_0 is ideal glass transition pressure and $A = \text{constant}$.

Equation (2) was derived from the Doolittle equation [26] $\tau = \tau_0 \exp(A'/V_f)$, in which $V_f \sim \kappa(p_0 - p)$ was substituted for the free volume, where κ is the isothermal compressibility coefficient.

In our recent paper, we indicated the applicability of yet another relation [27]:

$$\tau = \tau_0 \exp\left(\frac{Bp}{p_0 - p}\right). \quad (3)$$

This relation, equation (3), has the very natural property that τ_0 is a relaxation time for atmospheric pressure ($\tau = \tau_0$ for $T = \text{constant}$ and $p \rightarrow 0$). For isothermal measurements, starting from atmospheric pressure, the value of the relaxation time τ_0 is known. In this case, equation (3) contains only two unknown parameters, B and p_0 , which can be found from a fitting. Notice that relations (2) and (3) give the same values for the ideal glass transition pressure p_0 , because p_0 is defined by the divergence of the relaxation time.

Figures 2(a) and 2(b) present $\log_{10}(\tau_p)$ versus pressure for the pure compounds and for their mixtures, respectively. Solid lines show the quality of the fit, in agreement with equation (3).

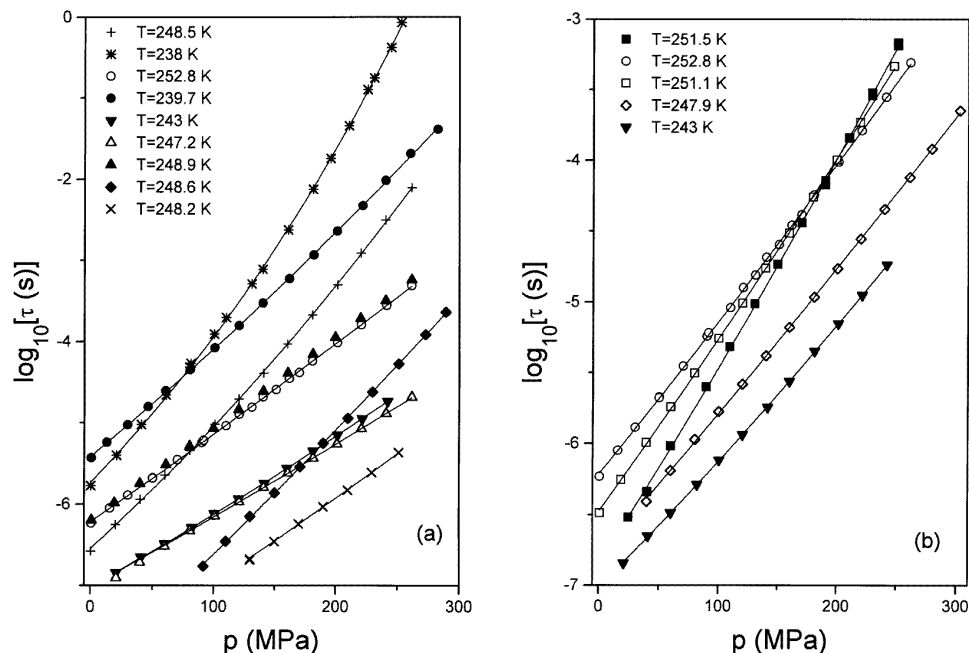


Figure 2. (a) $\log_{10}[\tau_p]$ (s) versus p for the following phthalate derivatives: di-isobutyl phthalate (stars and plus signs); bis(2-ethylhexyl) phthalate (open and solid circles); dibutyl phthalate (solid upright triangles); pentyl phthalate (open upright triangles); di-isonyl phthalate (solid upright triangles); diethyl phthalate (solid diamond symbols); and diallyl phthalate (crosses). (b) $\log_{10}[\tau_p]$ (s) versus p for the following solutions: (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19} (solid squares); (dimethyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5} (open squares); and (dibutyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5} (open diamond symbols). The data sets for bis(2-ethylhexyl) phthalate and dibutyl phthalate are presented for comparison. The solid lines are plots of equation (4), with the parameters given in table 1.

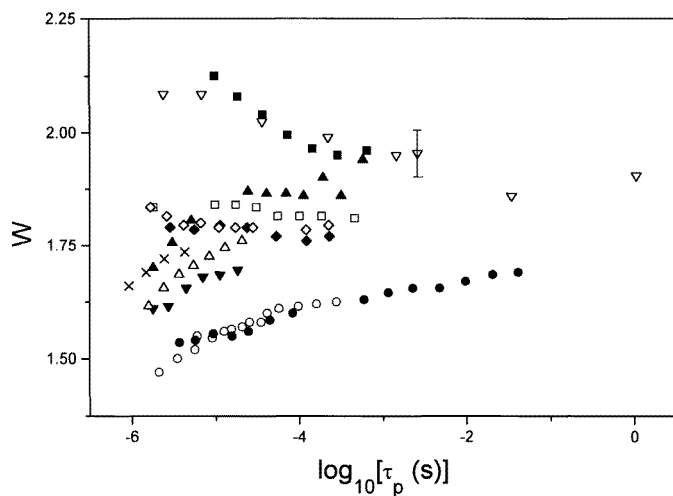
In table 2, the values of the parameters p_0 , τ_0 , and B obtained from the fitting of equation (3) to the data shown in figures 2(a) and 2(b) are compiled.

For di-isonyl phthalate, an almost linear pressure dependence of $\log_{10}(\tau_p)$ is observed; the fitting by means of equation (3) to the data gives an unphysical (very large) value of p_0 . Therefore, the fitting parameters for this sample were omitted from table 2. This kind of pressure dependence can be eventually described by an activation form (the pressure version of an Arrhenius relation) [20, 27].

In figure 2(b) one can notice that the tangents of the $\log_{10}(\tau_p)$ versus p curve for mixtures of different concentrations are contained between tangents of the curves given for single-component liquids. The results obtained for the full width at half-maximum W of the susceptibility curves as functions of temperature and pressure are very interesting. In some cases, W increases with the increase of the relaxation times, which is a typical phenomenon. In the case of (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19}, the full width at half-maximum of ϵ'' seems to decrease with the increase of the relaxation times for both isothermal and isobaric measurements. Figure 3 presents W versus $\log_{10}(\tau_p)$ for all of the systems tested. Moreover, in the case of the mixture (dibutyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5}, W has an almost constant value, independent of the relaxation

Table 2. Fitting parameters obtained from equation (3) for the data in figure 2(a) and figure 2(b).

Glass former	T_0 (K)	p_0 (MPa)	B	$\log_{10}[\tau_0$ (s)]
Bis(2-ethylhexyl) phthalate	252.8 ± 0.1	5560 ± 1300	135 ± 33	-6.214 ± 0.007
	239.7 ± 0.1	2450 ± 230	72 ± 7	-5.411 ± 0.009
Di-isobutyl phthalate	248.5 ± 0.1	1461 ± 100	47 ± 4	-6.54 ± 0.01
	238 ± 0.1	895 ± 30	33 ± 1.5	-5.73 ± 0.02
Diethyl phthalate	248.6 ± 0.1	3170 ± 640	101 ± 23	-8.04 ± 0.03
Dibutyl phthalate	243 ± 0.1	2610 ± 230	51 ± 5	-7.012 ± 0.005
Dipentyl phthalate	247.2 ± 0.1	4640 ± 1000	89 ± 21	-7.01 ± 0.01
Diallyl phthalate	248.2 ± 0.1	2400 ± 830	50 ± 20	-7.89 ± 0.06
(Dimethyl phthalate) _{0.81} + (bis(2-ethylhexyl) phthalate) _{0.19}	251.5 ± 0.1	3130 ± 600	97 ± 20	-6.85 ± 0.02
(Dimethyl phthalate) _{0.5} + (bis(2-ethylhexyl) phthalate) _{0.5}	251.1 ± 0.1	4300 ± 830	118 ± 24	-6.476 ± 0.008
(Di-isobutyl phthalate) _{0.5} + (bis(2-ethylhexyl) phthalate) _{0.5}	247.9 ± 0.1	4780 ± 990	106 ± 23	-6.77 ± 0.01

**Figure 3.** The full width at half-maximum W versus $\log_{10}[\tau_p$ (s)] for all of the systems tested, for both isothermal and isobaric measurements. The symbols are the same as in figure 2(a), figure 2(b), and figure 4. The size of the error bar is typical for all data sets.

times, in contrast to the case for the pure compounds, for which W clearly increases with the increase of the relaxation times. Similar behaviour was observed previously for other supercooled mixtures [28]. Apart from this, W is greater for this mixture, for fixed relaxation time, than for pure liquids. In each case one absorption peak was observed.

It is worth noticing that dimethyl phthalate crystallizes very easily. However, in a mixture with (2-ethylhexyl) phthalate it preserves the supercooled state over a wide range of pressures and temperatures.

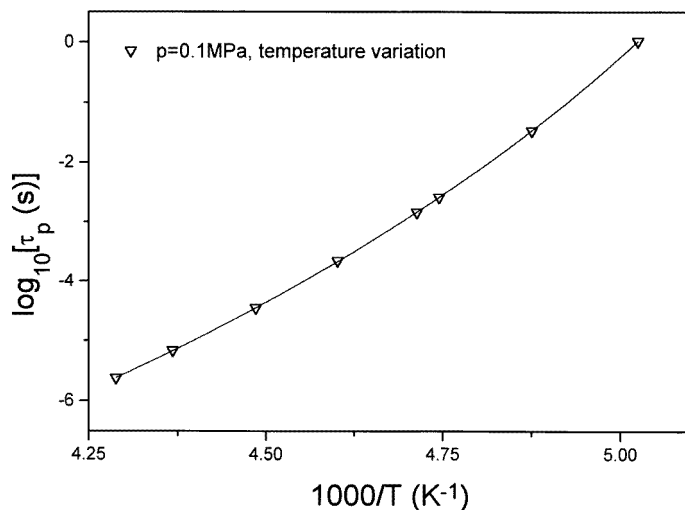


Figure 4. $\log_{10}[\tau_p$ (s)] versus the inverse of the absolute temperature for (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19}. The solid line is a fit according to the VFT equation.

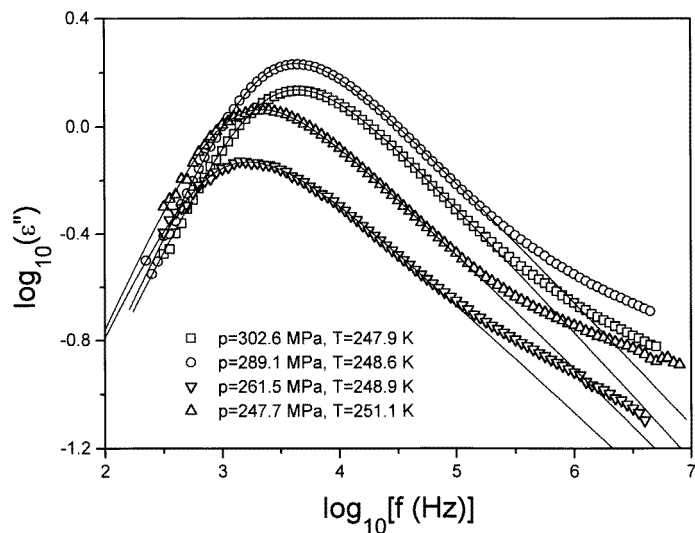


Figure 5. The imaginary part of the dielectric susceptibility of (dibutyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5} (squares); diethyl phthalate (circles); di-isonyl phthalate (upturned triangles); and (dimethyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5} (upright triangles). The solid line is a fit according to the Havriliak–Negami equation. The high-frequency β -relaxation process appears.

For (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19}, the dependence of the relaxation time on the inverse of the temperature under atmospheric pressure is shown in figure 4. These data obey the temperature Vogel–Fulcher–Tammann law

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

with the following fitting parameters: $T_0 = 145.7$ K and $B = 1770$ K.

Figure 5 shows the dependence of a few loss peaks on the frequency, $\varepsilon''(f)$, for diethyl phthalate, di-isonyl phthalate, (dimethyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5}, and (dibutyl phthalate)_{0.5} + (bis(2-ethylhexyl) phthalate)_{0.5}, with the values of the pressure fixed. In all cases, for high frequencies, β -relaxation appears. The solid lines present the Havriliak–Negami function [29] obtained from the fitting.

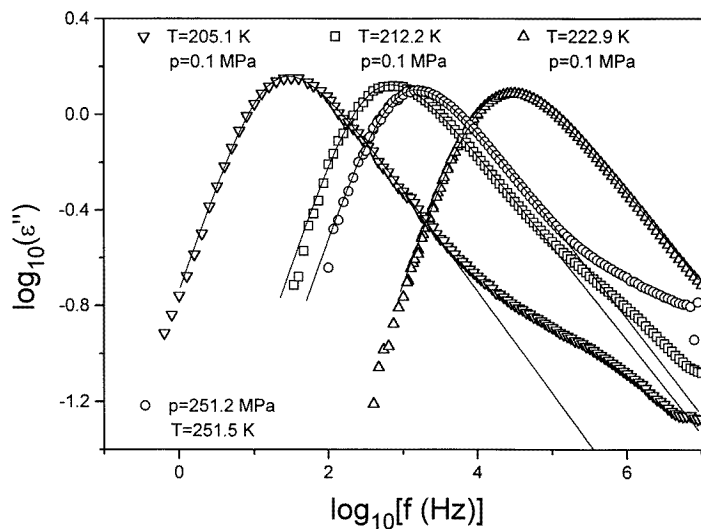


Figure 6. The dependence of ε'' on the frequency for the mixture (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19} for three isotherms under atmospheric pressure. The shape of ε'' under high pressure is also presented. Note that the pressure enhances the β -relaxation more than the decrease in temperature does.

In figure 6, the dependence of ε'' on the frequency for the mixture (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19} for several isotherms under atmospheric pressure is shown. In the same figure, the shape of ε'' for pressure $p = 251.2$ MPa and temperature $T = 251.5$ K is presented. Comparing these curves, the fact that pressure significantly enhances the β -relaxation can be easily seen. This fact has an influence on the scaling of the loss peaks. The results from applying a Dixon scaling to the absorption curves obtained from the pressure measurements for all of the samples and for the temperature measurements carried out on (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19} are presented in figure 7. In this case, in the high-frequency region a divergence between the temperature and pressure data was noticed. This can undoubtedly be associated with the greater strength of the β -relaxation process for the pressure path. The fact that pressure seems to enlarge the amplitude of the β -relaxation more than the equivalent temperature change is in our opinion one of the most significant conclusions of the studies presented.

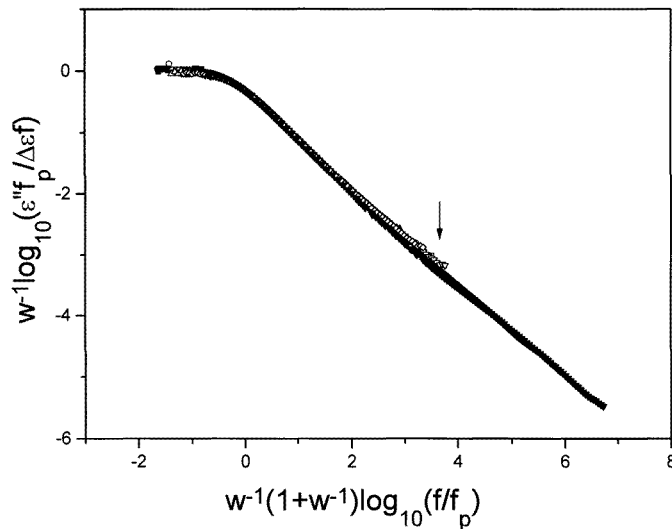


Figure 7. A Dixon scaling plot for the pressure and temperature dielectric relaxation data for (dimethyl phthalate)_{0.81} + (bis(2-ethylhexyl) phthalate)_{0.19}. The arrow points to a divergence between the temperature and pressure data in the β -relaxation region.

4. Conclusions

The pressure behaviour of the complex electric permittivity in glass-forming phthalate derivatives has been studied. We have shown that, for the glass formers studied, the relaxation times obey the relation $\tau = \tau_0 \exp(Bp/(p_0 - p))$ (equation (3)). The prefactor τ_0 obtained by fitting the pressure data with equation (3) is equal to the relaxation time under atmospheric pressure. Substituting the relaxation time under atmospheric pressure into equation (3) reduces the number of independent parameters from three to two. We have also tested the influence of high pressure on the dielectric absorption spectrum. The analysis of the absorption curves shows that pressure increases the amplitude of the β -relaxation more than the equivalent temperature change. It was found that Dixon scaling distinguishes isothermal measurements from isobaric measurements by means of the greater strength of the second relaxation process (β) for the pressure path. Our observations may be helpful in discussing the molecular origin of the β -relaxation process, which is not yet clarified.

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