PHYSICAL REVIEW E **75**, 011903 (2007)

Dielectric relaxation of α-tocopherol acetate (vitamin E)

K. Kaminski, S. Maslanka, J. Ziolo, and M. Paluch[*]
Institute of Physics, Silesian University, Universytecka 4, 40-007 Katowice, Poland

K. J. McGrath
Department of Chemistry, George Mason University, Fairfax, Virginia 22030, USA

C. M. Roland[†]
Chemistry Division, Code 6120, Naval Research Laboratory, Washington, District of Columbia, 20375-5342, USA

(Received 26 July 2006; published 8 January 2007)

Dielectric loss spectra are reported for α-tocopherol acetate (an isomer of vitamin E) in the supercooled and glassy states. The α-relaxation times, τ_α, measured over a 190° range of temperatures, T, at pressures, P, up to 400 MPa can be expressed as a single function of $TV^{3.9}$ (V is specific volume, measured herein as a function of T and P). At ambient pressure, there is no dynamic crossover over eight decades of measured τ_α. The relaxation spectra above the glass transition temperature T_g show ionic conductivity and an excess wing on the high-frequency flank of the α-relaxation loss peak. Temperature-pressure superpositioning is valid for the α process; moreover, the peak shape is constant (stretch exponent equal to 0.65). However, application of pressure changes the shape of the dielectric spectrum at higher frequencies due to the shift of the excess wing to form a resolved peak. Additionally, another relaxation process, absent at atmospheric pressure, emerges on the high-frequency side of the α-process. We propose that this new peak reflects a more compact conformation of the α-tocopherol acetate molecule. Drawing on the coupling model, the experimentally determined relaxation times, activation energy, and activation volume for the Johari-Goldstein process are compared to values calculated from the properties of the α relaxation. The agreement is generally satisfactory, at least for $T<T_g$.

DOI: 10.1103/PhysRevE.75.011903 PACS number(s): 87.15.He, 77.22.Gm, 64.70.Pf

I. INTRODUCTION

In recent years there has been increasing interest in dielectric relaxation measurements among pharmaceutical scientists [1–5]. Dielectric spectroscopy is an important tool for investigating the molecular mobility of vitrifying liquids, enabling observation of the dynamics of molecular dipoles over many decades of frequency. This characterization of the amorphous phase is relevant not only to manufacturing and storage, but even affects dosage through the latter's dependence on the physical and chemical stability of the pharmaceutical.

The majority of solid drugs are utilized in the crystalline state, associated with an ordered lattice structure. The state is generally thermodynamically stable and relatively simple to study. Some pharmaceuticals are prepared in an amorphous form [6–8]. The high internal energy and specific volume of the amorphous state relative to the crystal enhances dissolution and bioavailability [9], as well as chemical reactivity [10]; these features can improve product performance. However, the physical structure of glassy materials is more difficult to characterize, affecting quality assurance. Amorphous material may also be thermodynamically unstable, with a tendency to crystallize on storage [11,12]. An understanding of the nature and characterization of the glassy state and glass transition behavior is essential to realizing the predictability and stability of amorphous pharmaceuticals necessary for their optimal utilization.

Since the amorphous state is usually thermodynamically metastable relative to the crystalline form, the potential for crystallization during handling and storage may be present. This has lead to a number of studies of this problem. Fukuoka *et al.* [11] and Yoshioka *et al.* [12] showed that crystallization can take place even below the glass transition temperature T_g in dry amorphous indomethacin (a nonsteroidal anti-inflammatory drug). Hancock *et al.* [13] concluded from enthalpy recovery experiments that glassy indomethacin still exhibits significant molecular mobility, leading to crystallization. Alie *et al.* [14] showed that the crystal growth process in SSR, a low-molecular-weight model drug compound, is controlled by intramolecular dynamics involving the β-relaxation mode, rather than the motions involving all atoms in the molecule responsible for the α relaxation above T_g. Hancock and Zografi [15] also showed that trace levels of water may plasticize the sample sufficiently to bring the T_g value below the storage temperature, whereby crystallization commences. Usually this crystallization is undesirable, so commonly a high-T_g glass former such as PVP is cosolidified to stabilize an amorphous drug by raising the T_g of the binary mixture [16,17].

In this paper we present broadband dielectric relaxation and pressure-volume-temperature (PVT) data on α-tocopherol acetate measured at ambient and at elevated pressure. α-tocopherol acetate is the most biologically active of the eight isomers composing vitamin E, an essential human nutrient reputed to have anticancer properties. Recent studies have suggested this compound may induce apoptosis (arrest of uncontrolled cell proliferation) in a variety of epithelial cancer cell types [18]. The relaxation spectra at atmospheric pressure of α-tocopherol acetate are similar to com-

---

[*] Electronic address: mpaluch@us.edu.pl

[†] Electronic address: roland@nrl.navy.mil

1539-3755/2007/75(1)/011903(7)

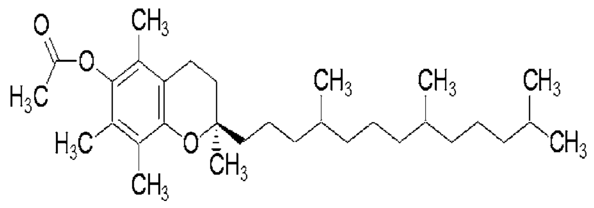

FIG. 1. Chemical structure of α-tocopherol acetate, the most biologically active isomer of vitamin E.

mon molecular glass-forming substances, showing the structural α relaxation with both an excess wing and a γ relaxation; however, the dielectric spectra measured for elevated pressure exhibit an additional process on the high-frequency flank of the α-relaxation peak. These secondary relaxation processes can serve as a mechanism for localized nucleation and consequent crystallization [19–21]; thus, their analysis is directly relevant to the use of amorphous pharmaceuticals. One result of the appearance of secondary relaxations at elevated pressure is a breakdown of temperature-pressure superpositioning of the structural α-relaxation peak; that is, while recent studies have shown that at a fixed value of τ_α (representing widely different combinations of temperature and pressure), the α peak for most glass formers is constant [22,23], in the case of α-tocopherol acetate, the emergence of a new relaxation process, obscured at low pressure, changes the apparent shape of this relaxation peak.

II. EXPERIMENTAL

The α-tocopherol acetate, purchased from Merck and used as received, has the chemical structure shown in Fig. 1. Ambient pressure measurements were performed in the frequency range from 10^{-2} to 10^{6} Hz using a Novocontrol Alpha dielectric spectrometer, with the sample in a parallel plate cell (diameter 20 mm, gap 0.1 mm). Temperature control of better than 0.1 K was achieved using a dry-nitrogen thermostated flow. For the high-pressure measurements the capacitor filled with the test material was placed in the high-pressure chamber and compressed using silicone fluid via a piston in contact with a hydraulic press (SITEC). The sample capacitor was sealed and mounted inside a Teflon ring to separate it from the silicone oil. Pressure was measured by a Nova Swiss tensometric meter (resolution ~0.1 MPa) and temperature controlled to 0.1 K by means of liquid flow from a thermostatic bath. PVT measurements were carried out with a Gnomix apparatus, with volume changes determined isothermally from 10 to 200 MPa over a temperature range from 300 to 360 K. The data were converted to specific volumes, V, using the value of V measured for ambient conditions with a pycnometer. A TA Instrument Q100 with liquid nitrogen cooling was employed for scanning calorimetry at 10 K/min.

III. RESULTS AND DISCUSSION

A. Ambient pressure

From cooling at 10 K/min, the calorimetric glass transition temperature of α-tocopherol acetate is 223 K. Representative dielectric loss spectra measured above T_g and at 0.1 MPa are shown in Fig. 2. There is a dc conductivity from mobile ionic contaminants and the prominent α peak (structural relaxation), both spectral features moving toward lower frequencies as T decreases. The shape of the α peak is essentially invariant to temperature. In Fig. 3, three spectra measured below T_g have been shifted along the frequency axis, superposing with the spectra for 235 K (although the overlap is primarily on the high-frequency side). We fit these superimposed peaks to the one-sided Fourier transform of the Kohlrausch-Williams-Watts (KWW) function [24,25],

$$\phi(t) = \exp[-(t/\tau_\alpha)^{\beta_{KWW}}], \quad 0 < \beta_{KWW} \leq 1 \qquad (1)$$

with the best-fit stretch exponent $\beta_{\mathrm{KWW}}=0.65$. A deviation of the fit is noted on the high-frequency side of the α peak; this

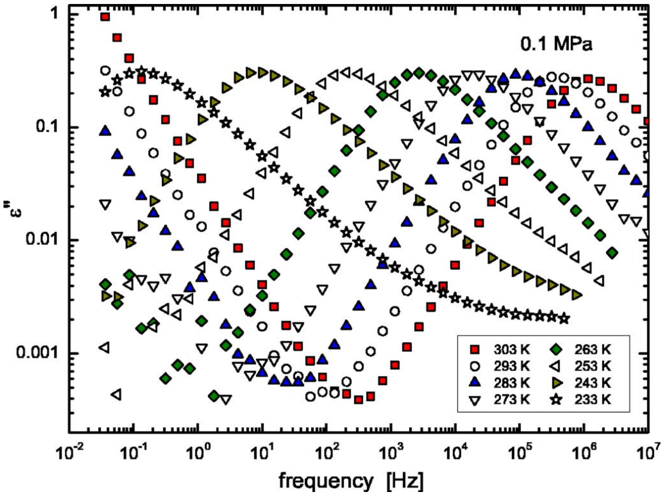

FIG. 2. (Color online) Dielectric loss curves for α-tocopherol acetate at the indicated temperatures and ambient pressure.

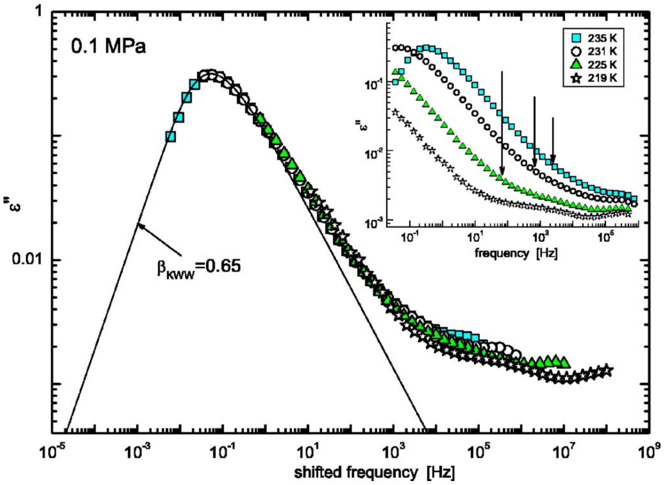

FIG. 3. (Color online) Ambient pressure dielectric loss spectra shifted along the abscissa to superpose the high-frequency side of the α peak. The solid line is the fit to the transform of Eq. (1), with $\beta_{KWW}=0.65$. In the inset are the same spectra as measured; the arrows denote the frequencies of the JG relaxation ($=1/2\pi\tau_{\mathrm{JG}}$) calculated from Eq. (2).

extra loss is the well-known excess wing of the structural relaxation. Various experiments including high-pressure measurements [26,27], physical aging [28,29], and mixtures with another glass former [30] have all shown unambiguously that the excess wing is the Johari-Goldstein (JG) secondary relaxation [31,32]. The JG relaxation is a specific secondary process having intermolecular character and seeming to serve as the precursor to the α relaxation [26]; thus, it has an important role in vitrification. When the JG relaxation time, τ_{JG} is close to τ_α, the JG peak is obscured by the dominant α peak and only appears as an excess wing.

To verify that the properties of the excess wing in α-tocopherol acetate are consistent with those of a JG relaxation, we apply the coupling model (CM) [33] to calculate τ_{JG} from the values of τ_α and β_{KWW} for the α relaxation using [26,34],

$$\tau_{JG}(T,P) \approx t_c^{1-\beta_{KWW}}[\tau_\alpha(T,P)]^{\beta_{KWW}}, \tag{2}$$

where t_c=2 ps for molecular and polymeric glass formers [35]. These calculated JG relaxation times are shown in the inset to Fig. 3 (indicated by arrows corresponding to $(2\pi\tau_{\mathrm{JG}})^{-1}$). The frequencies of the JG relaxation predicted by Eq. (2) fall within the vicinity of the (broad) excess wing, supporting the identification of the latter as an unresolved JG process. Equation (2) can be rewritten as [36]

$$\Delta = (1-\beta_{KWW})(\log \tau_\alpha + 11.7), \tag{3}$$

which makes explicit that the separation in frequency of the α and JG peaks, Δ, is governed (inversely) by the magnitude of β_{KWW}; that is, larger Δ for broader α peaks. Similar behavior is seen with eugenol (β_{KWW}=0.68), isoeugenol (β_{KWW}=0.62) [37], dioctyl phthalate (β_{KWW}=0.65) [38], and tripropylene glycol (β_{KWW}=0.63) [39]. All have narrow α dispersions ($\beta_{KWW}>0.6$) and thus exhibit an excess wing rather than a distinct, resolved secondary peak.

Although structural relaxation is arrested at the glass transition, the JG process exhibits activated behavior below T_g, giving rise to greater separation between the two peaks. This is shown in the loss spectra measured for $T<T_g$ (Fig. 4). With decreasing temperature, the excess wing becomes resolved as a distinct peak. At low temperatures another secondary relaxation, which we refer to as the δ process, appears at higher frequencies. This presumably is due to pendant group (intramolecularly correlated) motion.

Figure 5 shows the relaxation map for α-tocopherol acetate. The structural relaxation times can be described over the entire measured range with a single Vogel-Fulcher-Tamman-Hesse equation [40–42]

$$\tau_\alpha(T) = \tau_{\infty,\alpha} \exp\left(\frac{DT_0}{T-T_0}\right) \tag{4}$$

with $\tau_{\infty,\alpha}=2.40\times10^{-13}$ s, D=773, and T_0=173 K. There is no evidence of a change in dynamics ("dynamic crossover") [43–45] over the more than eight decades of τ_α. A modest extrapolation of the data using Eq. (4) yields T_g=226 K, defined as the temperature at which τ_α equals 100 s. This close to the calorimetric glass transition of 223 K. The steepness or "fragility" index $(\equiv d\log\tau_\alpha/d(T_g/T)|_{T_g})$, reflecting the rapidity of the change of τ_α in the supercooled regime, is equal to 63. Thus, α-tocopherol acetate is an intermediate glass former, although the narrowness of its α peak (β_{KWW}=0.65) is more in accord with that of strong liquids [46].

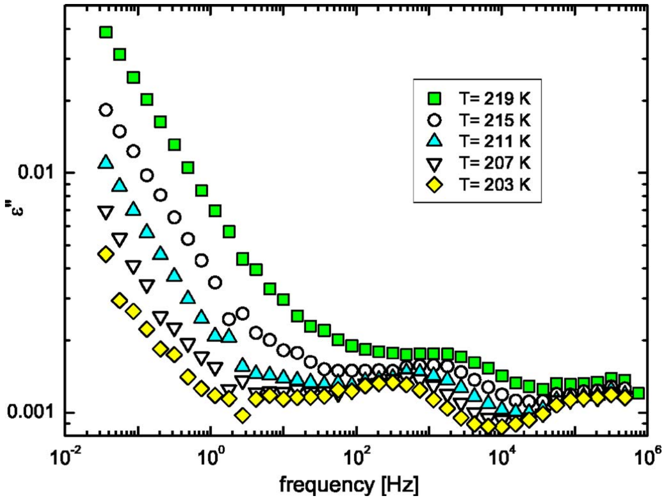

FIG. 4. (Color online) The frequency dependence of the dielectric loss ε'' at five temperatures below T_g.

To describe the two secondary peaks, the loss spectra below T_g were fit to a superposition of two Cole-Cole functions [47]. For both processes, the obtained relaxation times exhibit Arrhenius behavior (Fig. 5). For the δ relaxation, the prefactor $\tau_{\infty,\delta}=3\times10^{-11}$ s and $E_\delta=17\pm2$ kJ/mol; the small activation energy is consistent with motion of only some atoms in the α-tocopherol acetate molecule. For the JG relaxation, $\tau_{\infty,JG}=4.9\times10^{-14}$ s and the activation energy $E_{JG}=39.7\pm0.6$ kJ/mol. Various proposals have been made relating the magnitude of the JG activation energy to prop-

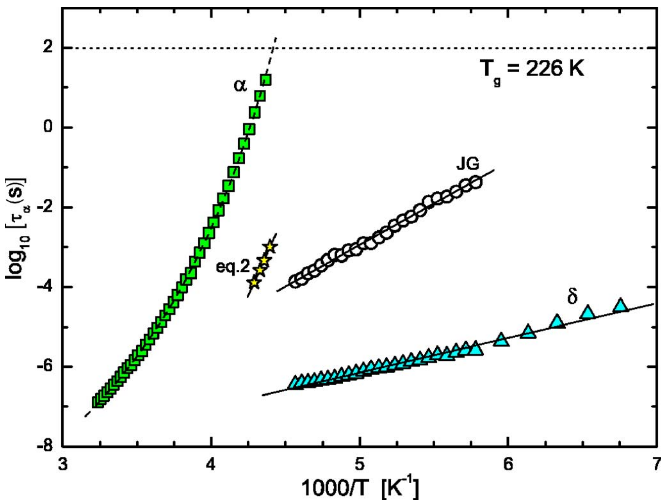

FIG. 5. (Color online) Arrhenius plot of the relaxation times for the α (squares), JG (circles), and δ process (triangles). Stars represent τ_{JG} for the liquid state calculated using Eq. (2) with β_{KWW}=0.65. Dashed line is the fit of τ_α to Eq. (4), while solid lines are linear fits of the secondary relaxation data. The uncertainty in the secondary relaxation times is on the order of the symbol size.

TABLE I. Activation energy for τ_{JG}.

	Experimental ($T<T_g$)	Eq. (5) ($T=T_g$)	Eq. (7) ($T\leq T_g$)	Eq. (6) ($T<T_g$)
E_{JG} (kJ/mol)	39.7±0.6	175	45	46

erties of the α relaxation. According to the CM [48,49] the ratio of the respective activation energies for τ_β and τ_α should equal the value of β_{KWW} describing the α peak,

$$E_{JG} = E_\alpha \times \beta_{KWW}. \tag{5}$$

This equation follows directly from Eq. (2). The activation energy of the α-process is non-Arrhenius, but at T_g we obtain from Eq. (4) an apparent $E_\alpha = 270$ kJ/mol. Equation (5) then gives a predicted value of E_{JG} that is more than a factor of 4 larger than the experimental result for the glassy state. Consistent with this result, τ_{JG} calculated from Eq. (2) for $T>T_g$ (shown in Fig. 5) exhibits a substantially steeper Arrhenius slope than the JG relaxation times measured for $T<T_g$. The calculated JG relaxation times are also larger in magnitude than the experimental τ_{JG}, and by an amount exceeding the uncertainties (which are *ca.* 50% or less).

A related CM prediction for τ_{JG} in the glassy state is [50]

$$E_{JG} = 2.303RT_g(13.7\beta_{KWW} - \log_{10}\tau_{\infty,JG} - 11.7), \tag{6}$$

from which we calculate an activation energy for τ_{JG} in the glassy state that is about 16% larger than measured. Equation (6) is similar to an empirical relation due to Kudlik *et al.* [51],

$$E_{JG} = 24RT_g, \tag{7}$$

which overestimates the experimental E_{JG} for $T<T_g$ by 13%. These various results are collected in Table I. Although the value from Eq. (5) for the liquid is not accurate, both Eqs. (6) and (7) yield E_{JG} that are close to the JG activation energy measured for the glass. It is known that in the vicinity of T_g, JG relaxation times become more sensitive to temperature [52–55]; for sorbitol and xylitol, for example, the activation energy for τ_β above T_g is ~40% larger than E_{JG} in the glassy state [52]. This may account for some of the difference between the predictions of Eqs. (5) and (6).

B. Elevated pressure

Dielectric measurements were carried out for elevated pressures at $T=298$ and 253 K, with representative spectra shown in Fig. 6. In addition to the usual shift of the relaxations toward lower frequencies with increasing P, a new process (which we designate the β' peak) appears on the high-frequency side of the α peak. As a result, ambient and elevated pressure spectra obtained at respective temperatures such that τ_α is constant (Fig. 7) do not superpose. This breakdown of superpositioning is at odds with the usual result that the frequency dispersion of the α relaxation together with the excess wing are invariant for widely different combinations of P and T, provided the α-peak frequency does not change [22,23]. However, this absence of superpositioning for α-tocopherol acetate is due to the pressure-induced emergence of a new relaxation peak.

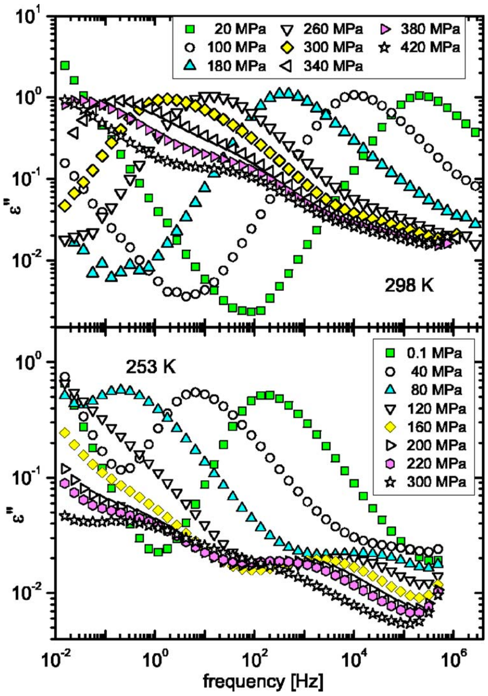

FIG. 6. (Color online) Dielectric loss spectra measured at $T=298$ K at various pressures from 20 MPa to 420 MPa (upper panel), and at $T=253$ K in the pressure range from 0.1 MPa to 300 MPa (lower panel).

As seen in Fig. 6, the relaxation time of this β' process is insensitive to pressure. The peak amplitude decreases with pressure, even though the peak itself becomes more visible in the spectra. The latter is the result of a strong diminution of the amplitude of the α-relaxation dispersion with pressure. From dielectric measurements alone, we cannot deduce the

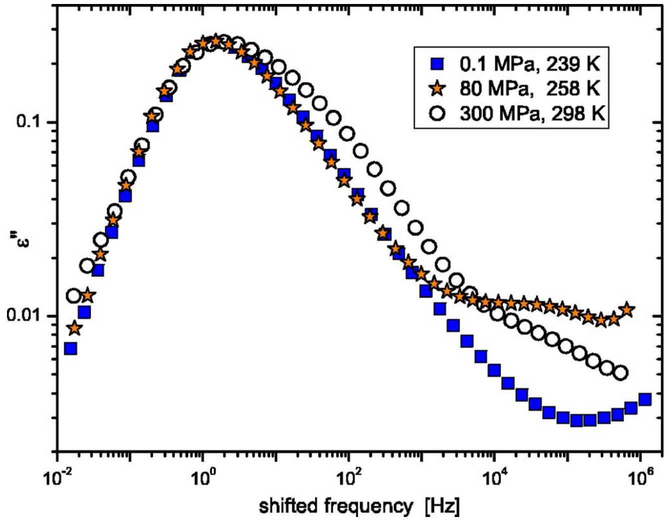

FIG. 7. (Color online) Dielectric loss spectra at 0.1 MPa and 239 K (squares), 80 MPa and 258 K (stars), and 300 MPa and 298 K (circles), showing the apparent change in shape of the α peak due to the emergence of the β' relaxation at high pressure.

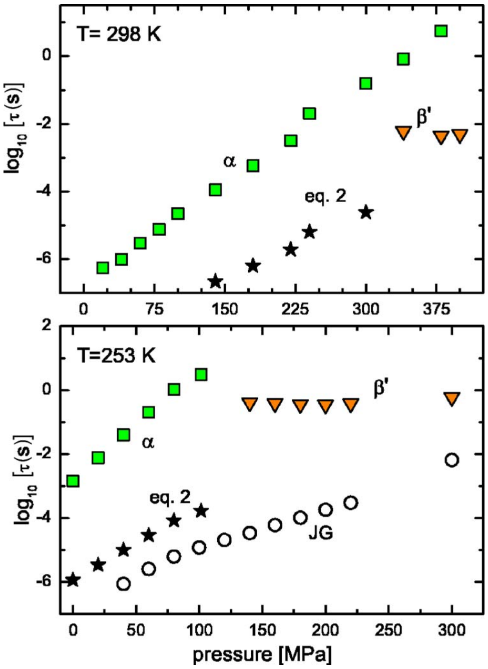

FIG. 8. (Color online) The relaxation times for the α (squares), JG (circles), and β' process (inverted triangles) as a function of pressure at $T=298$ K (upper panel) and $T=253$ K (lower panel). Stars represent τ_{JG} calculated using Eq. (2) with $\beta_{KWW}=0.65$.

origin of this β' relaxation. One possibility is that the application of hydrostatic pressure generates a meta phase, involving greater molecular compaction; i.e., a conversion of trans to gauche conformers (see Fig. 1), with a more compact structure exhibiting faster dynamics. Although evidence for this meta phase might be expected in the PVT data, those measurements do not extend to sufficiently high pressures (>325 MPa for $T=298$ K) or low temperatures ($T=253$ K for $P<200$ MPa).

In the data of Fig. 6 for 253 K, the excess wing can be seen to emerge as a resolved peak due to the stronger P dependence of the α peak (although the excess wing has some sensitivity to pressure, consistent with its identity as a JG process). The relaxation times measured at $T=253$ and 298 K are plotted vs pressure in Fig. 8 (note for 298 K the uncertainty is too large to yield reliable values for τ_{JG}). This P dependence can be characterized by an activation volume, defined as $\Delta V=RT\,(\partial \ln \tau/\partial P_T)|$. While $\Delta V_{\beta'}\sim 0$, the activation volume for the α and JG relaxations are substantial, $=157\pm 8$ and 83 ± 4 ml/mol, respectively. From the CM, the two quantities are related by an expression analogous to Eq. (5),

$$\Delta V_{JG}=\Delta V_{\alpha}\times \beta_{KWW}, \tag{8}$$

which overestimates the experimental ΔV_{JG} by 23%, which is significant. This small discrepancy is seen in the values of τ_{JG} calculated using Eq. (2) (Fig. 8), which are slightly steeper than the experimental data (in addition to being a factor of 10 larger).

A useful way to analyze the combined T and P dependences is to determine the variation in τ_{α} with the product TV^{γ}, in which γ is a material constant (independent of T, P, and V) [56,57]. The exponent on the specific volume is a measure of the contribution of volume (density) to the supercooled dynamics relative to the effect of temperature. It has been shown for more than 50 glass formers that τ_{α} is a unique function of TV^{γ} [57,58], with γ related to the steepness of the intermolecular repulsive potential [59,60].

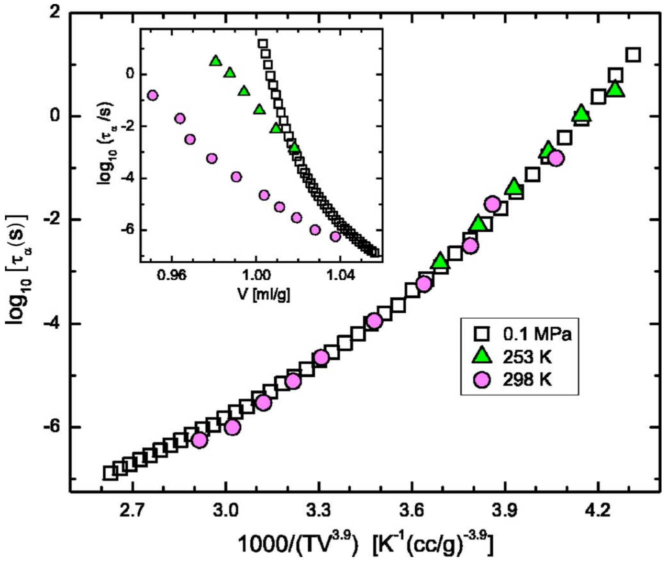

FIG. 9. (Color online) The α-relaxation times (two isotherms and an isobar) vs the product of temperature and specific volume, with the latter raised to the power of 3.9. The inset shows the same data as a function of specific volume.

We calculate the specific volume for any T and P from the equation of state for α-tocopherol acetate. The latter was obtained by fitting the PVT data to the Tait equation [61],

$$V(T,P)=V(T,0)(1-C\ln[1+P/B(T)]), \tag{9}$$

with $C=0.0894$ and the temperature dependence at ambient pressure given by

$$V(T,0)=1.0312+0.00067T+8.429\times 10^{-7}T^{2} \tag{10}$$

in units of ml/g and temperature in Celsius. The pressure dependence (in units of MPa) was described by

$$B(T)=183\exp(-4.44\times 10^{-3}T). \tag{11}$$

The α-relaxation times are plotted in Fig. 9 as a function of the scaling variable TV^{γ}, with $\gamma=3.9$ yielding superposition. This is a typical value for liquids having a bulky structure [58,62]. A more traditional measure of the contribution of volume and temperature to the dynamics is the relative magnitude of the isochoric, $(E_{\alpha})_V$, and isobaric, $(E_{\alpha})_V$, activation enthalpies [58,63,64]. This ratio varies from 0 (jammed, or volume-dominated, dynamics) to unity (thermally activated relaxation). Using the relation [56,65]

$$(E_{\alpha})_V/(E_{\alpha})_P=(1+\gamma\alpha_P T)^{-1}, \tag{12}$$

where α_P is the isobaric thermal expansion coefficient ($=5.896\times 10^{-4}$ K^{-1} at T_g and 0.1 MPa), we calculate $(E_{\alpha})_V/(E_{\alpha})_P=0.66$ at $T_g=226$ K. This is large for a molecular glass former, but emphasizes that both volume and temperature govern the dynamics, with a stronger effect from the latter. The volume dependence of τ_α *per se* is shown in the inset to Fig. 9.

IV. SUMMARY

Dielectric relaxation measurements were carried out on an isomer of vitamin E at both ambient and elevated pressure. The α relaxation has a peak shape that is invariant to thermodynamic conditions, apart from the separation of an excess wing for longer τ_α. The α peak is rather narrow ($\beta_{KWW}=0.65$), even though α-tocopherol acetate is a moderately fragile glass former. At low temperature and high pressure, two new secondary relaxations (δ and β') are observed. The former involves motion of only a part of the molecule (thus its high frequency), while the latter likely reflects development with P of a more compact molecular structure. The α-relaxation times superpose when plotted vs $TV^{3.9}$, in accord with behavior common to unassociated liquids and polymers. From the value of the scaling exponent, =3.9, we calculate an activation enthalpy ratio $E_V/E_P=0.66$ at T_g, indicating that temperature exerts a somewhat stronger influence on $\tau_\alpha(T)$ than does volume.

From τ_α and the magnitude of the stretch exponent, we use the coupling model to calculate properties of the JG relaxation. The predicted τ_{JG} are consistently larger, by about an order of magnitude, than values deduced from the frequency of the maximum of the JG peak, although the calculated τ_{JG} fall within the range of the broad JG dispersion. The JG activation energy measured for the glass and the experimental JG activation volume are both close to values calculated from the CM, which in turn is consistent with an empirical relation between E_{JG} and T_g. For the liquid state the CM overestimates the activation energy, although quantitative determination of E_{JG} for $T>T_g$ is problematic given the proximity of τ_{JG} and τ_α.

ACKNOWLEDGMENTS

The work at NRL was supported by the Office of Naval Research and at Silesian University by the Polish Committee for Scientific Research (KBN Grant No. 1 PO3B 075 28).

[1] L. Gunawan, G. P. Johari, and R. M. Shanker, Pharm. Res. **23**, 967 (2006).

[2] G. P. Johari and D. Pyke, Phys. Chem. Chem. Phys. **2**, 5479 (2000).

[3] E. Tombari, S. Preston, G. P. Johari, and R. M. Shanker, J. Pharm. Sci. **95**, 1006 (2006).

[4] L. Carpentier, R. Decressain, S. Desprez, and M. Descamps, J. Phys. Chem. B **110**, 457 (2006).

[5] V. Andronis and G. Zografi, Pharm. Res. **15**, 835 (1998).

[6] J. K. Haleblian, J. Pharm. Sci. **64**, 1269 (1975).

[7] S. R. Byrn, *Solid-State Chemistry of Drugs* (Academic Press, London, 1982).

[8] L. Yu, Adv. Drug Delivery Rev. **48**, 27 (2001).

[9] R. Huttenrauch, Acta Pharm. Technol. Suppl. **6**, 55 (1978).

[10] M. J. Pikal, A. L. Lukes, J. E. Lang, and K. Gaines, J. Pharm. Sci. **67**, 767 (1978).

[11] E. Fukuoka, M. Makita, and S. Yamamura, Chem. Pharm. Bull. (Tokyo) **34**, 4314 (1986).

[12] M. Yoshioka, B. C. Hancock, and G. Zografi, J. Pharm. Sci. **83**, 1700 (1994).

[13] B. C. Hancock, S. L. Shamblin, and G. Zografi, Pharm. Res. **12**, 799 (1995).

[14] J. Alie, J. Menegotto, P. Cardon, H. Duplaa, A. Caron, C. Lacabanne, and M. Bauer, J. Pharm. Sci. **93**, 218 (2004).

[15] B. C. Hancock and G. Zografi, Pharm. Res. **11**, 471 (1994).

[16] E. Fukuoka, M. Makita, and S. Yamamura, Chem. Pharm. Bull. (Tokyo) **37**, 1047 (1989).

[17] M. Yoshioka, B. C. Hancock, and G. Zografi, J. Pharm. Sci. **84**, 983 (1995).

[18] K. Kline, W. Yu, and B. G. Sanders, J. Nutr. **134**, 3458S (2004).

[19] G. Power and J. K. Vij, J. Chem. Phys. **120**, 5455 (2004).

[20] O. Norimaru and M. Oguni, Solid State Commun. **99**, 53 (1996).

[21] S. Tomikata, M. Mizukami, F. Paladi, and M. Oguni, J. Therm Anal. Calorim. **81**, 637 (2005).

[22] C. M. Roland, R. Casalini, and M. Paluch, Chem. Phys. Lett. **367**, 259 (2003).

[23] K. L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, and C. M. Roland, J. Phys. Chem. B **109**, 17356 (2005).

[24] R. Kohlrausch, Ann. Phys. (Leipzig) **12**, 393 (1947).

[25] G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[26] K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).

[27] R. Casalini and C. M. Roland, Phys. Rev. B **69**, 094202 (2004).

[28] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **84**, 5560 (2000).

[29] K. L. Ngai, P. Lunkenheimer, C. Leon, U. Schneider, R. Brand, and A. Loidl, J. Chem. Phys. **115**, 1405 (2001).

[30] T. Blochowicz, *Broadband Dielectric Spectroscopy in Neat and Binary Molecular Glass Formers* (Logos Verlag, Berlin, 2003).

[31] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[32] G. P. Johari, J. Non-Cryst. Solids **307–310** 317 (2002).

[33] K. L. Ngai, J. Phys. Condens. Matter **15**, S1107 (2003).

[34] C. León, K. L. Ngai, and C. M. Roland, J. Chem. Phys. **110**, 11585 (1999).

[35] K. L. Ngai and R. W. Rendell, in *Supercooled Liquids, Advances and Novel Applications*, edited by J. T. Fourkas, D. Kivelson, U. Mohanty, and K. Nelson, ACS Symposium Series Vol. 676 (American Chemical Society, Washington, DC, 1997).

[36] K. L. Ngai, J. Chem. Phys. **109**, 6982 (1998).

[37] E. Kaminska, K. Kaminski, M. Paluch, and K. L. Ngai, J.

Chem. Phys. **124**, 164511 (2006).
[38] E. Kaminska, K. Kaminski, S. Hensel-Bielowka, M. Paluch, and K. L. Ngai, J. Non-Cryst. Solids **352**, 4672 (2006).
[39] R. Casalini and C. M. Roland, Phys. Rev. B **69**, 094202 (2004).
[40] H. Vogel, Phys. Z. **22**, 645 (1921).
[41] G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1925).
[42] G. Tammann and W. Hesse, Z. Anorg. Allg. Chem. **156**, 245 (1926).
[43] F. Stickel, E. W. Fischer, and R. Richert, J. Chem. Phys. **104**, 2043 (1996).
[44] R. Casalini and C. M. Roland, Phys. Rev. Lett. **92**, 245702 (2004).
[45] R. Casalini, M. Paluch, and C. M. Roland, J. Chem. Phys. **118**, 5701 (2003).
[46] R. Bohmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
[47] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
[48] K. L. Ngai and C. M. Roland, Macromolecules **27**, 2454 (1994).
[49] C. Leon, K. L. Ngai, and A. Rivera, Phys. Rev. B **69**, 134303 (2004).
[50] K. L. Ngai and S. Capaccioli, Phys. Rev. E **69**, 031501 (2004).
[51] A. Kudlik, S. Benkhof, T. Blochowicz, C. Tschirwitz, and E. Rossler, J. Mol. Struct. **479**, 201 (1999).
[52] M. Paluch, C. M. Roland, S. Pawlus, J. Zioło, and K. L. Ngai, Phys. Rev. Lett. **91**, 115701 (2003).
[53] H. Wagner and R. Richert, J. Phys. Chem. B **103**, 4071 (1999).
[54] T. Fujima, H. Frusawa, and K. Ito, Phys. Rev. E **66**, 031503 (2002).
[55] R. Nozaki, H. Zenitani, A. Minoguchi, and K. Kitai, J. Non-Cryst. Solids **307–310**, 349 (2002).
[56] R. Casalini and C. M. Roland, Phys. Rev. E **69**, 062501 (2004).
[57] C. M. Roland and R. Casalini, J. Non-Cryst. Solids **351**, 2581 (2005).
[58] C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).
[59] C. M. Roland, J. L. Feldman, and R. Casalini, J. Non-Cryst. Solids **352**, 4895 (2006).
[60] R. Casalini, U. Mohanty, and C. M. Roland, J. Chem. Phys. **125**, 014505 (2006).
[61] P. Zoller and D. J. Walsh, *Standard Pressure-Volume-Temperature Data for Polymers*, (Technomic Publishing Company, Lancaster, PA, 1995).
[62] C. M. Roland, S. Bair, and R. Casalini, J. Chem. Phys. **125**, 124508 (2006).
[63] C. M. Roland, M. Paluch, T. Pakula, and R. Casalini, Philos. Mag. **84**, 1573 (2004).
[64] G. Williams, in *Dielectric Spectroscopy of Polymeric Materials*, edited by J. P. Runt and J. J. Fitzgerald (American Chemical Society, Washington, DC, 1997).
[65] R. Casalini and C. M. Roland, Colloid Polym. Sci. **283**, 107 (2004).