

Relation between the α -Relaxation and Johari–Goldstein β -Relaxation of a Component in Binary Miscible Mixtures of Glass-Formers

S. Capaccioli

Dipartimento di Fisica and INFN (UdR Pisa), Università di Pisa, Largo B. Pontecorvo 3, I-56127 Pisa, Italy, and INFN CRS “SOFT: Complex Dynamics in Structured Systems”, Università di Roma “La Sapienza”, Piazzale Aldo Moro 2, I-00185 Roma, Italy

K. L. Ngai*

Naval Research Laboratory, Washington, D.C. 20375-5320

Received: November 8, 2004; In Final Form: February 14, 2005

The coupling model was applied to describe the α -relaxation dynamics of each component in perfectly miscible mixtures $A_{1-x}B_x$ of two different glass-formers A and B. An important element of the model is the change of the coupling parameter of each component with the composition, x , of the mixture. However, this change cannot be determined directly from the frequency dispersion of the α -relaxation of each component because of the broadening caused by concentration fluctuations in the mixture, except in the limits of low concentrations of either component, $x \rightarrow 0$ and $x \rightarrow 1$. Fortunately, the coupling model has another prediction. The coupling parameter of a component, say A, in the mixture determines τ_α/τ_{JG} , the ratio of the α -relaxation time, τ_α , to the Johari–Goldstein (JG) secondary relaxation time, τ_{JG} , of the same component A. This prediction enables us to obtain the coupling parameter, \hat{n}_A , of component A from the isothermal frequency spectrum of the mixture that shows both the α -relaxation and the JG β -relaxation of component A. We put this extra prediction into practice by calculating \hat{n}_A of 2-picoline in binary mixtures with either tri-styrene or *o*-terphenyl from recently published broadband dielectric relaxation data of the α -relaxation and the JG β -relaxation of 2-picoline. The results of \hat{n}_A obtained from the experimental data show its change with composition, x , follows the same pattern as assumed in previous works that address only the α -relaxation dynamics of a component in binary mixtures based on the coupling model. There is an alternative view of the thrust of the present work. If the change of \hat{n}_A with composition, x , in considering the α -relaxation of component A is justified by other means, the theoretical part of the present work gives a prediction of how the ratio τ_α/τ_{JG} of component A changes with composition, x . The data of τ_α and τ_{JG} of 2-picoline mixed with tri-styrene or *o*-terphenyl provide experimental support for the prediction.

1. Introduction

Explaining the changes of dynamics of a component in a binary miscible mixture of two glass-formers from that in the neat state is a challenging problem. The binary miscible mixtures in which we are interested in this work are restricted to those which are miscible down to the molecular length scale without cluster formation of any kind and/or supramolecular ordering, do not phase separate, and have no specific interaction between the two kinds of molecules at all compositions. A successful explanation based on the extension of a model or theory for a neat glass-former is most desirable. There are many studies of miscible mixtures of two glass-formers on the changes of the primary α -relaxation of either component.^{1–5} Seldom seen is the study of the effects of mixing on both the primary α -relaxation and the secondary β -relaxation in parallel, particularly when the secondary relaxation of one of the glass-formers is intermolecular in origin (i.e., a Johari–Goldstein relaxation).^{6–8} There are only a few examples from dielectric measurements of the kind of miscible mixtures in which we are interested. The systems include mixtures of water with glycol oligomer,⁹ alcohol,¹⁰ glycerol,¹¹ sorbitol,¹² and glucose;¹³ mix-

tures of glycerol with sorbitol;¹⁴ and mixtures of 2-picoline with tri-styrene.^{15,16} For polymers, there are blends of poly(vinyl methyl ether) with poly(2-chlorostyrene),¹⁷ poly(*n*-butyl methacrylate-*stat*-styrene) copolymers,^{18,19} and poly(4-vinylphenol)/poly(ethyl methacrylate) blends.²⁰ These studies reported a change of the dynamics of both the primary and secondary relaxation of a component in binary blends. For a theoretical interpretation of the dynamics in these works, one needs an approach that can address not only the change of the α -relaxation dynamics but also that of the secondary relaxation of the Johari–Goldstein (JG) kind.

Among secondary relaxations,²¹ the Johari–Goldstein (JG) β -relaxation^{6–8} is the most important for glass transition because it has properties suggesting that it is the local step or the precursor of the α -relaxation. Certainly, the secondary relaxations observed in totally rigid molecular glass-formers are appropriately called JG β -relaxations after the researchers who found them. A more stringent definition of JG β -relaxation extended to nonrigid glass-formers has recently been proposed in ref 21.

As far as we know, among theories or models of the dynamics of neat glass-formers, the coupling model^{22–25} is the only approach that has been extended to address the α -relaxation

* Email address: ngai@estd.nrl.navy.mil.

and the JG β -relaxation of a neat glass-former as well as the α -relaxation dynamics of a component in a binary miscible mixture. For the latter, it is natural to extend the model further to account simultaneously for the α -relaxation and the JG β -relaxation coming from the same component of a mixture and their changes with the composition of the mixture. Work in this direction has been started and applied to the sorbitol component in sorbitol/glycerol mixtures²⁶ and the xylitol component in xylitol/water mixtures.²⁷ These mixtures are hydrogen-bonded systems, and the component studied, sorbitol or xylitol, has already a resolved JG relaxation.

In this work, we extend the model in a different direction. We consider mixtures of van der Waals glass-forming liquids in the absence of hydrogen bonding and the dynamics of a component A which in its neat state has no resolved JG relaxation. Upon mixing this component with another component B with significantly lower mobility (e.g., higher T_g), from the extended coupling model, we show that a resolved JG relaxation of component A emerges. The separation in time scales of the α -relaxation and the JG relaxation, all coming from component A, increases monotonically with the concentration of component B. These predictions of this extended blend model are compared with experimental dielectric relaxation data.

2. Coupling Model Interpretation of α -Relaxation and JG Relaxation in Neat Glass-Formers

The coupling model (CM)^{22–25} emphasizes the many-molecule nature of the α -relaxation dynamics of a neat glass-former A through the intermolecular coupling of the relaxing species with others in its environment. Rigorous solution of a simple coupled system²³ has given support to the premise of the CM. Here, we restate in brief the physical basis of the CM before extending it to include the connection to the JG relaxations. The many-molecule α -dynamics are heterogeneous^{28,29} and complicated, and only averages over these heterogeneities are considered in the CM. The CM recognizes that all attempts of relaxation have the same primitive rate, τ_0^{-1} , but the many-molecule dynamics prevent all attempts of molecules to be simultaneously successful, resulting in faster and slower relaxing molecules or heterogeneous dynamics. However, when averaged, the effect is equivalent to the slowing down of τ_0^{-1} by another multiplicative factor, which is time dependent. The time-dependent rate, $W(t)$, has the product form $\tau_0^{-1}f(t)$, where $f(t) < 1$. In particular, it has to be

$$W(t) = \tau_0^{-1}(\omega_c t)^{-n} \quad (1)$$

with $0 \leq n < 1$, in order for the solution of the averaged rate equation to be the empirical Kohlrausch stretched exponential function

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}] \quad (2)$$

Here, n is the coupling parameter of the CM and $\beta \equiv (1 - n)$ is the fractional Kohlrausch exponent. More important are the many-molecule dynamics or the extent of the dynamic heterogeneity, larger is the coupling parameter, n , and vice versa. The time-dependent rate, $\tau_0^{-1}(\omega_c t)^{-n}$, also leads immediately to the most important relation between τ_α and τ_0 of the CM given by

$$\tau_\alpha = (t_c^{-n} \tau_0)^{1/(1-n)} \quad (3)$$

after identifying t_c introduced here by $t_c = (1 - n)^{-(1/n)}/\omega_c$. Many-molecule dynamics cannot start instantly. In fact, from

experiments and molecular dynamics simulations of polymeric and small molecular liquids performed at short times, the Kohlrausch function no longer holds at times shorter than approximately 2×10^{-12} s and is replaced by the linear exponential time dependence of the primitive relaxation. This property indicates that t_c is equal to 2 ps.

The CM described above has recently been extended to make the connection of its primitive relaxation time, τ_0 , with the most probable relaxation time of the Johari–Goldstein relaxation.^{24–26,30–33} Such a connection is expected from the similar characteristics of the two relaxation processes including (1) their local nature, (2) involvement of the entire molecule, and acting as the precursor of the α -relaxation. Multidimensional NMR experiments^{34,35} have shown that in the systems studied molecular reorientation in the heterogeneous α -relaxation (executed by the primitive relaxation in the CM) occurs by relatively small jump angles, just like in the JG relaxation.³⁶ Since it may seem that there is now another role played by the primitive relaxation, *separate and distinctive* from that described in the above for the Kohlrausch α -relaxation, it is necessary to give the following clarifications. At short times, when there are few independent relaxations present, they appear separately in space as localized motions just like the JG relaxation. Hence,

$$\tau_{JG}(T) \approx \tau_0(T) \quad (4)$$

and this is one role played by the independent relaxation. At times beyond τ_0 or τ_{JG} , more units can independently relax, they cannot be considered as isolated events anymore, and some degree of cooperativity (or dynamic heterogeneity) is required for motions to be possible. The degree of cooperativity and the corresponding length scale continues to increase with time as more and more units participate in the motion, as suggested by the evolution of the dynamics of colloidal particles with time obtained by confocal microscopy.³⁷ These time evolving processes contribute to the observed response at times longer than τ_0 or τ_{JG} and are responsible for the broad dispersion customarily identified as the JG relaxation by most workers. Within this popular definition of the JG relaxation, an experiment performed to probe it will find that “essentially” all molecules contribute to the JG relaxation and the dynamics are dynamically and spatially heterogeneous as found by dielectric hole burning³⁸ and deuteron NMR³⁹ experiments. This description of the JG relaxation may help to resolve the difference between two different points of view on its nature.^{8,36} After sufficiently long times, $t \gg \tau_0$ or τ_{JG} , *all* units attempt the primitive relaxation, and the *fully* cooperative α -relaxation regime (described before in the first paragraph of this section) having the maximum dynamic heterogeneity length scale, L_{dh} , and the Kohlrausch form for the averaged correlation function at the temperature is reached. Naturally, we expect a larger L_{dh} is associated with a larger n , as borne out by comparing L_{dh} for glycerol, *o*-terphenyl, and poly(vinyl acetate) obtained by multidimensional ¹³C solid-state exchange NMR experiments.⁴⁰

The CM merely accounts for the effect of the complex many-molecule dynamics, slowing the relaxation from τ_0 to τ_α via eq 2. The dependences of the relaxation on temperature, entropy, and volume enter first into τ_0 and are amplified in τ_α because of the raising to the power given by the superlinear exponent, $1/(1 - n)$, in eq 2. Evidence that τ_0 already senses the specific volume (or free volume) and entropy (or configurational entropy) comes from that of τ_{JG} of the JG relaxation. They include (1) the relaxation time, τ_{JG} ,^{15,31,41} as well as the relaxation strength, $\Delta\epsilon_{JG}$,⁷ of the JG relaxation showing changes

of temperature dependence at T_g ; (2) the shift of τ_{JG} to longer times by physical aging;^{32,42} and (3) the dependence of τ_{JG} on pressure.⁴³

3. α -Relaxation of a Component in Binary Mixtures

Before discussing theoretically the component dynamics in binary mixtures, it is necessary to define the mixtures to which the theoretical framework applies. They are supposed to be miscible down to the molecular length scale without cluster formation of any kind and/or supramolecular ordering and do not phase separate and have no significant specific interaction between the two kinds of molecules at all compositions. Since this paper also addresses the experimental data of mixtures of 2-picoline with tri-styrene or *o*-terphenyl, we give more information on them as an example of the kind of binary mixture of interest in this study.

Derivatives of pyridine (like picoline), although classified as strongly hydrogen-bonded solvents, can dissolve the weakly polar systems such as polystyrene. Calculations based on three-component solubility parameters provide a degree of solubility of polystyrene in pyridine derivatives similar to that of good solvents commonly used for polystyrene including benzene, ethylbenzene, ethylacetate, or toluene.⁴⁴ The homogeneous mixture picoline/tri-styrene is a solution of nonideal type with negative deviation. The molecules are randomly dispersed, and the mixture is homogeneous for any polystyrene concentration. Although at low temperatures a reduction of the entropy of mixing could induce a miscibility gap for some value of polystyrene concentration, nevertheless the low number of repeating units constituting tri-styrene (and OTP) favors miscibility of this oligomer contrary to what could happen for high molecular weight polystyrene. In fact, the osmotic pressure forces emerging from the translational motion of the oligomers are stronger than the local molecular interactions. Thus, the large contribution due to translational entropy makes the Gibbs free energy of mixing strongly negative and these systems do not exhibit demixing at lower temperatures, as shown by calorimetric measurements in ref 16. The α -relaxation of each component in such miscible mixtures of two glass-formers has its own dynamics, which change with the composition of the blend. The first direct evidence came from solid-state ^{13}C MAS NMR measurements on 1,4-polyisoprene (PIP)/polyvinylethylene (PVE) blends.⁴⁵ The solid-state ^{13}C MAS NMR technique allows the components of a blend to be differentiated by their isotropic chemical shifts. Combined mechanical and dielectric spectroscopies were also used to probe the component dynamics in this same blend,⁵⁰ yielding results in quantitative agreement⁵¹ with subsequent deuterium NMR measurements.⁴⁶ The dynamics of the 2-picoline component in mixtures with tri-styrene or *o*-terphenyl are exclusively probed by dielectric measurement because of the negligible dipole moment of tri-styrene and *o*-terphenyl. Thus, the mixtures considered in the present study, as well as other perfectly miscible binary mixtures of van der Waals liquids and polymer blends, are good candidates for testing the coupling model predictions presented below.

Perhaps the first published model addressing the component α -dynamics of binary mixtures A/B was by an application of the CM.^{47–52} This approach extends the coupling model for neat glass-formers to mixtures by incorporating other sources of heterogeneity of dynamics in mixtures, due to the intrinsic mobility differences of the components (i.e., τ_{0A} and τ_{0B} of the neat A and neat B molecules are different) and to the local compositional heterogeneity coming from concentration fluctuations. In the mixture, the intrinsic mobilities may be different

from τ_{A0} and τ_{B0} in the neat states and depend on the local composition. The α -relaxation dynamics (τ_A or τ_B) of a component (A or B) in a mixture are determined by its chemical structure as well as by the local environment, since the latter governs the intermolecular coupling and the many-molecule dynamics determining the α -relaxation. The environments for either component, say A, are not identical due to composition fluctuations. There is a distribution of environments, $\{i\}$, of the A molecules, which in turn engenders a distribution of independent relaxation times, $\{\tau_{Ai}\}$, and coupling parameters, $\{n_{Ai}\}$, for the A molecules.

To fix ideas, we consider from now on that the glass transition temperature of the neat A glass-former is much lower than that of the neat B glass-former, such that the intrinsic mobility of A is significantly higher than that of B, or $\tau_{A0} \ll \tau_{B0}$. In a mixture, before we account for intermolecular interaction and many-molecule dynamics necessary for the α -relaxation, a comparison of the intrinsic mobilities of A and B molecules has to be considered first. From the standpoint of the molecule A in the mixture $A_{1-x}B_x$, the partial replacement of A molecules by the intrinsically less mobile B molecules in its environment, *i*, will further slow the dynamically heterogeneous α -relaxation in which it is involved. In other words, the much less mobile B molecules impose more permanent constraints on the A molecule through interactions and slow the relaxation of the A molecule even more than when it is in the neat A glass-former. Hence, the coupling parameter, n_{Ai} , appearing in the averaged relaxation rate, $W_{Ai}(t) = \tau_{Ai}^{-1}(\omega_c t)^{-n_{Ai}}$, is increased over and above n_A of the neat A glass-former. There is clear experimental support of such an increase of n_{Ai} from data on reorientation of A molecules taken at very low concentrations such that the complication of concentration fluctuation in mixtures is absent. Indeed, the correlation function of the probe molecules A has a Kohlrausch time dependence (eq 2) and a larger coupling parameter that increases with a decrease of the ratio of the probe relaxation time to the longer relaxation time of the host molecules B (see Figure 2 of ref 53). Returning to our discussion on the mixture $A_{1-x}B_x$, thus all n_{Ai} in the distribution are larger than the coupling parameter, n_A , of the neat A glass-former, that is,

$$n_{Ai} > n_A \quad (5)$$

The differences between n_{Ai} and n_A become larger when there are more less mobile B molecules in the mixture. Equations 2 and 3 apply to each *i* in the distribution. For each *i*, the α -relaxation correlation function of A is given by

$$\phi_{Ai}(t) = \exp[-(t/\tau_{Ai})^{1-n_{Ai}}] \quad (6)$$

where n_{Ai} is its coupling parameter and τ_{Ai} is its cooperative α -relaxation times, and they are again related by the equation

$$\tau_{Ai} = [t_c^{-n_{Ai}} \tau_{0Ai}]^{1/n_{Ai}} \quad (7)$$

In the framework of the CM, effects of slowing down from all interactions including that arising from the intermolecular potential and dipole–dipole correlations are taken into account by n_{Ai} .

The observed dielectric response of all A molecules in the mixture is the superposition of the one-sided Fourier transforms of eq 6, each weighed by the probability of the occurrence of *i* in the distribution, $\{i\}$.^{47–52} Local composition richer in the less mobile B has larger n_{Ai} . In eq 7, the exponent $(1 - n_{Ai})$ is the dominant quantity that determines τ_{Ai} . Consequently, τ_{Ai}

of environment i with larger n_{Ai} is shifted to longer time and has a stronger temperature dependence. This effect causes broadening on the low frequency side of the dispersion which, in extreme cases, leads to a reversal of the asymmetry of the loss peak found in the neat A glass-former. Instead of skewing toward high frequency as in the one-sided Fourier transforms of Kohlrausch functions, the dispersion is altered to skewing toward lower frequency. Blends of PVME/PS and PVE and PIP exemplify this feature.^{47–50} The loss peak in the dielectric and dynamic mechanical spectrum in these blends is unusually broad and is strongly skewed toward lower frequency. Thus, the presence of composition fluctuation makes it difficult, if not impossible, to use the isothermal dielectric relaxation data of blends to prove unambiguously that n_{Ai} in the distribution are larger than the coupling parameter, n_A , of the neat A glass-former, that is, inequality 5. However, experimental proof is found in mixtures at a very low concentration of A molecules where composition fluctuation is absent. Indirect evidence comes from the observed increase of the fragility or steepness index, m , of component A in the blend.^{47–49,51} The increase of the coupling parameter is deduced from the empirical correlation between m and the coupling parameter.⁵⁴

The frequency dispersion is not the emphasis of this work and hence not discussed any further. Instead, we focus on the loss peak frequency, $f_{\alpha, \max} \equiv 1/(2\pi\tau_{\alpha, \max})$, which is determined by the contribution from the most probable ones, \hat{i} , of the distribution of environments in the mixture $A_{1-x}B_x$. Let us denote their coupling parameter by \hat{n}_A , the independent relaxation time by $\hat{\tau}_{A0}$, the α -relaxation time by $\hat{\tau}_{A\alpha}$, and the correlation function by

$$\hat{\phi}_A(t) = \exp[-(t/\hat{\tau}_{A\alpha})^{1-\hat{n}_A}] \quad (8)$$

Since $i = \hat{i}$ is just a special case, $\hat{\tau}_{A\alpha}$ can be calculated by eq 7, and it is given by the expression

$$\hat{\tau}_{A\alpha} = [t_c^{-\hat{n}_A} \hat{\tau}_{A0}]^{1/(1-\hat{n}_A)} \equiv \left(\frac{\hat{\tau}_{A0}}{t_c}\right)^{(\hat{n}_A/(1-\hat{n}_A))} \hat{\tau}_{A0} \quad (9)$$

Also, as a special case of inequality 5, the most probable coupling parameter, \hat{n}_A , of the mixture is larger than n_A , the coupling parameter of the neat glass-former A, that is,

$$\hat{n}_A > n_A \quad (10)$$

Upon increasing x , the concentration of the less mobile component B, \hat{n}_A increases due to enhanced intermolecular constraints. Since \hat{n}_A appears in the exponent in eq 9, it is the principal cause of the increase of $\hat{\tau}_{A\alpha}$ with x . Because \hat{i} has the highest probability of occurrence, the one-sided Fourier transform of eq 8 is largely responsible for determining the maximum of the observed α -loss peak frequency of component A in the mixture. Thus, the experimentally determined $\tau_{\alpha, \max}$ should correspond to the calculated $\hat{\tau}_{A\alpha}$ by eq 9. In the limit of $x \rightarrow 0$, the mixture $A_{1-x}B_x$ becomes the neat glass-former A, and eqs 8 and 9 are reduced to eqs 2 and 3, respectively.

Since $t_c \approx 2$ ps is very short, in most experiments, the ratio $(\hat{\tau}_{A0}/t_c)$ is much larger than unity in the entire temperature range of investigation. It follows immediately from eq 9 that $\hat{\tau}_{A\alpha}$ is much longer than $\hat{\tau}_{A0}$. The exponent $[\hat{n}_A/(1-\hat{n}_A)]$ in eq 9 follows \hat{n}_A to increase with x and is principally responsible for the rapid increase of $\hat{\tau}_{A\alpha}$ with an increase of x in the mixture $A_{1-x}B_x$ at constant temperature. Another contribution to the increase of $\hat{\tau}_{A\alpha}$ with an increase of x at constant temperature is the possible change of $\hat{\tau}_{A0}$, starting from τ_{A0} of neat A molecules

when $x = 0$. Combined in eq 9, these two effects, coming from the increases of \hat{n}_A and $\hat{\tau}_{A0}$ of component A in mixtures of increasing concentration of component B, constitute the CM for the α -relaxation of component A.^{47–52} So far, there is no direct experimental evidence from the spectra of the mixtures to bear out the increase of \hat{n}_A due to complication from composition fluctuation as discussed before. Nothing is known about the possible change of $\hat{\tau}_{A0}$ either. Fortunately, there is an additional relation between the primitive relaxation time and the Johari–Goldstein time (eq 4). When extended to the mixture, this relation enables us to obtain directly the change of $\hat{\tau}_{A0}$ and deduce \hat{n}_A from the isothermal dielectric relaxation data of the mixtures. This important advance and the main thrust of this work is presented in the following sections.

4. JG β -Relaxation of a Component in Mixtures

A recent advance of the coupling model for a neat glass-former is the connection between the Johari–Goldstein β -relaxation time, τ_{JG} , and the independent or primitive relaxation time, τ_0 .^{24,25} Experimental data on various single component glass-forming substances^{24,25,55,56} show remarkably good correspondence between τ_0 calculated by eq 3 from the parameters τ_α and n of the α -relaxation and τ_{JG} from experiment (see eq 4). In the mixtures $A_{1-x}B_x$, for component A, eq 3 is replaced by eq 9 and eq 4 by

$$\tau_{A,JG}(T) \approx \hat{\tau}_{A0}(T) \quad (11)$$

One may wonder how $\hat{\tau}_{A\alpha}$, $\hat{\tau}_{A0}$, and $\tau_{A,JG}$ can be obtained from experiment, particularly the assignment of the observed JG relaxation to component A. In dielectric relaxation experiments, this assignment is clear if the B molecule has a much smaller dipole moment compared with that of the A molecule. Thus, the observed α -relaxation and JG relaxation in the dielectric spectrum of the mixture originate from the A, and their relaxation times are for sure $\hat{\tau}_{A\alpha}$ and $\tau_{A,JG}$ of component A.

The correspondence between the observed JG relaxation time, $\tau_{A,JG}$, and the independent relaxation time, $\hat{\tau}_{A0}$, given by eq 11, allows us to substitute the experimentally determined JG relaxation time, $\tau_{A,JG}$, for $\hat{\tau}_{A0}$ in eq 9. Furthermore, we replace $\hat{\tau}_{A\alpha}$ by the experimentally determined most probable α -relaxation time, $\tau_{\alpha, \max}$, of component A in the mixture. Upon taking a logarithm of all quantities and recalling that $t_c \approx 2 \times 10^{-12}$ s, eq 9 can be rewritten as

$$\hat{n}_A = [\log(\tau_{\alpha, \max}) - \log(\tau_{A,JG})]/[\log(\tau_{\alpha, \max}) + 11.7] \quad (12)$$

Equation 11 enables us to calculate \hat{n}_A from the experimental quantities $\tau_{\alpha, \max}$ and $\tau_{A,JG}$. Hence, those $A_{1-x}B_x$ mixtures having both the α -relaxation and the JG relaxation of component A been measured at the same temperature can be used to test the principal hypothesis of the CM that \hat{n}_A increases monotonically with the concentration of the less mobile component B. Moreover, from eq 11, the measured $\tau_{A,JG}$ gives an estimate of the change of the primitive relaxation time, $\hat{\tau}_{A0}$, with the concentration of B molecules. These tasks will be carried out in the next section.

5. α -Relaxation and JG β -Relaxation of a Component in Mixtures

There are many glass-formers A which in the neat state do not show a resolved JG β -relaxation either in the equilibrium liquid state or the glassy state. Examples such as glycerol,^{57,58} propylene glycol,⁵⁹ propylene carbonate,^{41,57} cresol phthalate

dimethyl ether,⁶⁰ 2-picoline,^{15,16} and tri-styrene^{15,16} show no secondary relaxation whatsoever in the dielectric loss spectra at any temperature. There is however the excess wing appearing on the high frequency side of the α -loss peak. There are various evidences^{15,16,42,61–63} that this excess wing is the JG β -relaxation hidden under the dominant α -loss peak because τ_{JG} is not much shorter than $\tau_{\text{A}\alpha}$.^{15,16,21,24,25,55} From the coupling model eqs 3 and 4 and $t_c \approx 2 \times 10^{-12}$ s, the separation between the two relaxation times (in seconds) is given by

$$\log \tau_{\text{A}\alpha} - \log \tau_{\text{JG}} = n_{\text{A}}(\log \tau_{\text{A}\alpha} + 11.7) \quad (13)$$

This relation indicates that the separation is small if n_{A} is small or the stretch exponent $(1 - n_{\text{A}})$ of the Kohlrausch function, used to fit the α -relaxation of the neat glass-former A, is large. In fact, all the glass-formers A showing an excess wing but no other secondary relaxation have smaller n_{A} . As an aside, there are plenty of experimental data showing the excess wing shifts with pressure,⁶⁴ and hence also the hidden JG relaxation. The pressure dependence of the hidden JG relaxation in the equilibrium liquid state indicates that the dependence of molecular mobility on volume and entropy has already entered into the JG relaxation or the primitive relaxation of the CM, long before the birth of the α -relaxation after going through many-molecule dynamics.

Now consider such a glass-former A, having only an excess wing and a small n_{A} in its neat state. When mixed with a higher T_{g} glass-former B, the separation between the α -relaxation and the JG relaxation both originating from the A molecules is given via eq 12 by

$$\log \tau_{\text{A}\alpha, \text{max}} - \log \tau_{\text{A,JG}} = \hat{n}_{\text{A}}(\log \tau_{\text{A}\alpha, \text{max}} + 11.7) \quad (14)$$

The CM expects that $\hat{n}_{\text{A}} > n_{\text{A}}$, and \hat{n}_{A} increases monotonically with the concentration of B molecules in the mixture. Consequently, from eq 14, the separation between the JG β -relaxation and α -relaxation of component A should increase monotonically with the concentration of B molecules in the mixtures. Hence, at sufficiently high concentrations of B, the JG β -relaxation of A should become resolved from the usually more dominant α -relaxation. For any mixture in which the JG β -relaxation of A is resolved, we can use eq 14 to calculate \hat{n}_{A} from the experimental values of $\tau_{\text{A}\alpha, \text{max}}$ and τ_{JG} . This course of action is tantamount to using one coupling model prediction on the JG β -relaxation (eq 14) to support the description of component α -dynamics in mixtures principally from the increase of the coupling parameter of the α -relaxation, \hat{n}_{A} , in eq 9.

There are published dielectric relaxation measurements on mixtures with 2-picoline with tri-styrene or 2-picoline with *o*-terphenyl (OTP).^{15,16,65} In both cases, neat 2-picoline plays the role of the glass-former A that has only an excess wing but not a resolved JG β -relaxation and a small n_{A} value of 0.36. The dipole moments of tri-styrene and *o*-terphenyl are small compared with that of 2-picoline, and thus, the observed dielectric spectra of the mixtures are essentially entirely coming from the relaxations of the 2-picoline molecules. At about 20% tri-styrene, the excess wing changes to exhibit a shoulder indicating the emergence of JG β -relaxation.^{15,16} Above 30% tri-styrene, the JG β -relaxations are clearly seen in the loss spectra as resolved peaks. Their relaxation times, τ_{JG} , can be obtained directly from the isothermal dielectric loss data as the reciprocal of the angular frequency, $2\pi\nu_{\text{JG}}$, at the maximum of the JG β -loss peak. The distance between the α -relaxation and the JG β -relaxation of 2-picoline, $(\log \tau_{\text{A}\alpha, \text{max}} - \log \tau_{\text{JG}})$, increases with the percentage of tri-styrene for any chosen fixed

value of $\log \tau_{\text{A}\alpha, \text{max}}$. For example, Figure 2 of ref 15 shows such a trend at constant $\nu_{\text{A}\alpha, \text{max}} \approx 10^{-2}$ Hz for mixtures containing 60, 50, 40, and 25% 2-picoline. Via eq 14, this trend validates the expected monotonic increase of \hat{n}_{A} with the concentration of tri-styrene molecules in the mixture. Hence, the remarkable increase of the α -relaxation time, $\hat{\tau}_{\text{A}\alpha}$ or $\tau_{\text{A}\alpha, \text{max}}$, of 2-picoline when mixed with tri-styrene is adequately explained by eq 9 of the CM, principally through the monotonic increase of \hat{n}_{A} . The proposed increase of \hat{n}_{A} in considering the α -relaxation of component A in the mixture now has an independent check by calculating \hat{n}_{A} using another prediction of the coupling model, that is, eq 12, and a separate experimental quantity of 2-picoline in the mixtures, which is the distance between the α -relaxation and the JG β -relaxation. This check has been carried out, using the dielectric loss data shown in Figure 2 of ref 15 and additional data from ref 16. Some of the isothermal dielectric loss data of the mixtures containing 50, 40, and 25% 2-picoline in tri-styrene as well as 50 and 30% 2-picoline in *o*-terphenyl show well defined α -loss and JG β -loss peaks. These data allow us to determine directly the peak frequencies, $\nu_{\text{A}\alpha, \text{max}}$ and ν_{JG} , at several temperatures for each of these mixtures (see Table 1) and the corresponding relaxation times, $\tau_{\text{A}\alpha, \text{max}}$ and τ_{JG} , and hence $(\log \tau_{\text{A}\alpha, \text{max}} - \log \tau_{\text{JG}})$, without using any arbitrary assumed procedure to deduce them. The values of \hat{n}_{A} calculated by eq 12 for some of the mixtures are shown in Table 1, together with $n_{\text{A}} = 0.36$ of neat 2-picoline. The same results are depicted graphically in Figure 1, where the y-axis on the left representing $(\log \tau_{\text{A}\alpha, \text{max}} - \log \tau_{\text{JG}})$ is plotted against \hat{n}_{A} for picoline/tri-styrene (solid triangles) and for picoline/OTP (solid circles). The solid line and dashed line nearby are $(\log \tau_{\text{A}\alpha, \text{max}} - \log \tau_{\text{JG}})$ as a function of \hat{n}_{A} predicted by eq 12 for $\tau_{\text{A}\alpha, \text{max}} = 10^2$ and 10^3 s, respectively. The vertical line is drawn to indicate that $n_{\text{A}} = 0.36$ of neat 2-picoline. The monotonic increase of the coupling parameter, \hat{n}_{A} , of 2-picoline (in the most probable environments of the mixtures) with increasing content of tri-styrene or OTP is evident by inspection of Figure 1. The data of blends with more than 50% picoline do not show a resolved JG loss peak,^{15,16} and there is large uncertainty in the determination of τ_{JG} using any arbitrary fitting procedure. For this reason, they are not considered.

The treatment of the isothermal dielectric loss data of 5% picoline requires more explanation. At low temperatures of 170 K and below, when $\tau_{\text{A}\alpha, \text{max}}$ becomes so long that the entire α -relaxation of picoline has moved out of the experimental frequency window, the JG β -relaxation was observed as a very broad symmetric loss peak.¹⁶ The Arrhenius temperature dependence of $\tau_{\text{A,JG}}$ is given by $3 \times 10^{-15} \exp[27.27 \text{ (kJ/mol)/RT}]$.^{15,16} However, at the higher temperatures of 223 K and above, the α -loss peaks were seen but the measurements had not been carried out to sufficiently high frequencies to find the corresponding JG β -relaxation. To obtain the quantity $(\log \tau_{\text{A}\alpha, \text{max}} - \log \tau_{\text{A,JG}})$ at 220.2 K, the glass transition temperature determined by differential scanning calorimetry, we extrapolate the Arrhenius dependence of τ_{JG} at temperatures below T_{Ag} to determine $\log \tau_{\text{A,JG}}(T_{\text{Ag}})$ at $T_{\text{Ag}} \approx 220.2$ K. Approximately, we have $\log[\tau_{\text{A,JG}}(T_{\text{Ag}})/\text{s}] = -8.06$ and $\log[\tau_{\text{A}\alpha, \text{max}}(T_{\text{Ag}})/\text{s}] \approx 2$. The corresponding frequencies, $\nu_{\text{A}\alpha, \text{max}}$ and ν_{JG} , are given in Table 1. From them and eq 12, we deduce $\hat{n}_{\text{A}} = 0.73$. However, in extrapolating the Arrhenius dependence of $\tau_{\text{A,JG}}$ determined deep in the glassy state and below 170 K up to $T_{\text{Ag}} \approx 220.2$ K, large error can be made in obtaining $\tau_{\text{A,JG}}(T_{\text{Ag}})$. This is possible because the JG loss peak in the glassy state is very broad, having a full width at half-maximum of seven or more decades. Therefore, we consider another method to estimate \hat{n}_{A} at 220.2

TABLE 1: Experimental and Calculated Parameters of the α -Relaxation and the JG β -Relaxation of 2-Picoline in Binary Mixtures with Either Tri-styrene or *o*-Terphenyl (for details, see footnotes and text)^a

% of 2-picoline in tri-styrene	$\log(\nu_{\alpha,\max}/\text{Hz})$	$\log(\nu_{\text{AJG}}/\text{Hz})$	\hat{n}_A calculated from eq 12	τ_∞	$(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ T_{Ag} from DSC (ref 15)	$(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$ calculated from eq 19
5	-2.8	7.26 ^b	0.73 ^b	3×10^{-15}	14.5 ^b	14.9 ^b
5	-1.7	N/A	0.63 ^c	3×10^{-15}	14.5 ^c	17.3 ^c
25	-2.2	5.7	0.61	3×10^{-17}	23.1 ^d	22.9 ^d
25	-3.3	5.5	0.61	3×10^{-17}	23.1 ^e	23.9 ^e
25	-4.3	5.0	0.61	3×10^{-17}		24.8 ^f
40	-0.7	4.4	0.44	5×10^{-16}	g	g
40	-2.0	4.1	0.47	5×10^{-16}	26.0 ^h	24.1 ^h
40	-3.8	3.2	0.48	5×10^{-16}	26.0 ⁱ	25.9 ⁱ
50	-3.9	2.3	0.41	10^{-13}	25.0 ^j	23.1 ^j
100	-0.8	N/A	0.36	N/A	N/A	N/A

% of 2-picoline in OTP	$\log(\nu_{\alpha,\max}/\text{Hz})$	$\log(\nu_{\text{JG}}/\text{Hz})$	\hat{n}_A calculated from eq 12	τ_∞	$(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ T_{Ag} from DSC (ref 16)	$(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$ calculated from eq 19
30	-2.4	4.5	0.52	6×10^{-17}	25.5 ^k	25.3 ^k
30	-1.0	4.9	0.50	6×10^{-17}	l	l
50	-3.0	2.5	0.40	4×10^{-15}	26.5 ^m	25.4 ^m
100	-0.8	N/A	0.36	N/A	N/A	N/A

^a The experimental values of the ratio $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ taken from refs 15 and 16, were obtained by using the glass transition temperature determined by differential scanning calorimetry for T_{Ag} . On the other hand, in calculating the ratio $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$, we use the T_{Ag} determined from the dielectric loss peak frequency by the definition that $\log[\nu_{\alpha,\max}(T_{\text{Ag}})/\text{Hz}]$ has the value given on the same row of the table. If the difference between T_{Ag} from DSC and that from the dielectric $\log[\nu_{\alpha,\max}(T_{\text{Ag}})/\text{Hz}]$ is large, the experimental and calculated ratios are not compared. When the difference is not large, we enter $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ together with $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$ on the same row to make a comparison. See explanations given in footnotes b–m. N/A means that data are not available. ^b ν_{AJG} at 223 K (entry at third column) is obtained by extrapolation of the Arrhenius temperature dependence of ν_{AJG} determined deep in the glassy state, and from which \hat{n}_A is determined. The $T_{\text{Ag}} = 220.2$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is about 3 K lower than 223 K, the temperature at which the data in the second and fourth columns of this row were deduced and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^c At 5% picoline, the concentration fluctuation is not important, and \hat{n}_A is deduced from a fit of the dielectric loss data at 225 K by the one-sided Fourier transform of the Kohlrausch function. The $T_{\text{Ag}} = 220.2$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is about 5 K lower than 225 K, the temperature at which the data in the second and fourth columns of this row were deduced and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^d The $T_{\text{Ag}} = 185.2$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is slightly lower than the temperature 186 K at which the data in the first and third columns of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^e The $T_{\text{Ag}} = 185.2$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is slightly higher than the temperature 183 K at which the data in the first and third columns of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^f The temperature is 181 K at which the data in the first and third columns of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^g $\nu_{\alpha,\max}$ is too high at the temperature at which the data in the first and third columns of this row were taken, and the Arrhenius temperature dependence of ν_{AJG} no longer holds. For this reason, no comparison is made. ^h The $T_{\text{Ag}} = 167.5$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is about 3 K lower than the temperature at which the data of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ⁱ The $T_{\text{Ag}} = 167.5$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is nearly the same as the temperature at which the data of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^j The $T_{\text{Ag}} = 156.3$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is lower than the temperature 158 K at which the data of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^k The $T_{\text{Ag}} = 183.0$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is nearly the same as the temperature 182 K at which the data of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$. ^l $\nu_{\alpha,\max}$ is too high at the temperature at which the data in the first two columns of this row were taken, and the Arrhenius temperature dependence of ν_{AJG} no longer holds. For this reason, no comparison is made. ^m The $T_{\text{Ag}} = 161.1$ K value from DSC used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{exptl}}$ is lower than the temperature of about 164 K at which the data of this row were taken and used to calculate $(E_{\text{JG}}/RT_{\text{Ag}})_{\text{calcd}}$.

K. At 5% picoline, we assume that concentration fluctuation is not important and the fit to the α -loss spectrum by the one-sided Fourier transform of the Kohlrausch function gives directly \hat{n}_A . The lowest temperature at which complete loss peak data are available is 225 K, and the fit yields $\hat{n}_A = 0.63 \pm 0.02$. From the general trend that the width of the α -loss peak either increases or remains constant with decreasing temperature, we can consider $\hat{n}_A = 0.63 \pm 0.02$ as a lower bound to the actual value of \hat{n}_A at $T_{\text{Ag}} \approx 220.2$ K. The two values of \hat{n}_A and the corresponding values of $(\log \tau_{\alpha,\max} - \log \tau_{\text{AJG}})$ are shown in Table 1 and Figure 1. The uncertainty of the exact value of \hat{n}_A is due to the absence of data of both $\tau_{\alpha,\max}$ and τ_{AJG} at a common temperature, and not the limitation of the method. At 225 K, $\log(\nu_{\alpha,\max}/\text{Hz}) = -1.7$, and with $\hat{n}_A = 0.63$, the calculated value of $\log(\nu_{\text{AJG}}/\text{Hz})$ is 6.2 according to eq 12. However, the data were not taken beyond 10^5 Hz. The coupling parameter of the 5% picoline estimated by either method described above is large and is the largest among all the mixtures studied by Blochowicz et al. (see Table 1). This is certainly expected because of the preponderance of the less mobile tri-styrene molecules seen by the picoline in this mixture.

Models of component dynamics in binary miscible mixtures consider only the α -relaxation, and the main task is to explain

the change with composition of the molecular mobility or the temperature, T_{Ag} , of component A at which $\tau_{\alpha,\max}$ reaches an arbitrarily chosen long time. These kinds of models include the previous applications of the CM^{47–52} to miscible mixtures, where the explanation is based on the change of the coupling parameter, \hat{n}_A , in the mixture. For the component 2-picoline (A) in mixtures with tri-styrene or OTP, the increase of T_{Ag} with a decrease of the concentration of 2-picoline is explained in part by the monotonic increase of \hat{n}_A starting from $n_A = 0.36$ of neat 2-picoline. Since \hat{n}_A has been determined for several compositions of the mixtures from $(\log \tau_{\alpha,\max} - \log \tau_{\text{AJG}})$ in Figure 1, we find indeed that the increase of T_{Ag} is accompanied by a corresponding increase of \hat{n}_A . This is shown in Figure 1 by plotting $[T_{\text{Ag}}^{\text{B}} - T_{\text{Ag}}^{\text{A}}]/[T_{\text{g}}^{\text{B}} - T_{\text{g}}^{\text{A}}]$ as the y-axis on the right against \hat{n}_A . Here, T_{g}^{A} and T_{g}^{B} are the glass transition temperatures of neat 2-picoline and neat tri-styrene or OTP, respectively.

6. Other Properties of the α -Relaxation and JG β -Relaxation of a Component in Mixtures

After having proven the key premise of the CM that the most probable coupling parameter, \hat{n}_A , of the α -relaxation of component A does change with composition in the manner expected,

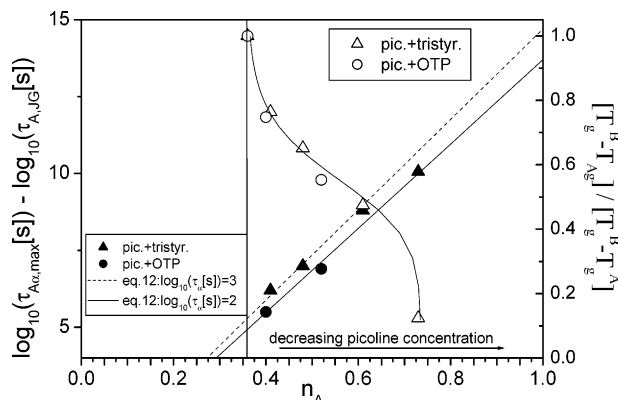


Figure 1. Left y-axis (solid symbols): separation between α-relaxation time and JG relaxation time evaluated at T_{Ag} versus the coupling parameter, \hat{n}_A . The data are from Table 1. From left to right, the solid triangles stand for data of 50, 40, 25, and 5% 2-picoline in tri-styrene and the solid circles stand for 50 and 30% 2-picoline in OTP. The behavior predicted by eq 12 is shown by the solid and dashed lines, \hat{n}_A evaluated at $\log(\tau_{A\alpha,\max}) = 2$ and $\log(\tau_{A\alpha,\max}) = 3$, respectively. The vertical line is drawn to indicate the value $\hat{n}_A = 0.36$ for the neat picoline system. Right y-axis (hollow symbols): a plot of $[T_g^B - T_g^A]/[T_g^B - T_g^A]$ against \hat{n}_A to show the increase of T_{Ag} , the glass transition temperature of 2-picoline in the mixtures, with decreasing concentration of 2-picoline versus the coupling parameter, \hat{n}_A . Here, T_g^A and T_g^B are the glass transition temperatures of neat 2-picoline and neat tri-styrene or OTP, respectively. The triangles represent data from the picoline/tri-styrene mixture, and the circles represent data from the picoline/OTP mixture. The concentrations of 2-picoline or \hat{n}_A are the same as those for the left y-axis. The sigmoid line is a guide to the eye.

we discuss other properties of the α-relaxation and JG β-relaxation of the same component in the remainder of this work.

(a) The Ratio $E_{JG}/(RT_{Ag})$ from the α-Relaxation and JG β-Relaxation of Component A in Mixtures. At temperatures below T_g , it is well-known that the most probable relaxation times of all JG β-relaxations of the neat glass-former A have Arrhenius temperature dependence.

$$\tau_{JG}(T) = \tau_{\infty} \exp(E_{JG}/RT), \quad T \leq T_g \quad (15)$$

where τ_{∞} is the prefactor, E_{JG} the activation enthalpy, and R the gas constant. The same is true for the JG relaxation time of component A in the mixtures $A_{1-x}B_x$.^{15,16}

$$\tau_{A,JG}(T) = \tau_{\infty} \exp(E_{JG}/RT) \quad (16)$$

We have previously shown for neat glass-formers, as a consequence of eq 12, that there is a relation between E_{JG} and T_g given by

$$E_{JG}/(RT_g) = 2.303(2 - 13.7n - \log \tau_{\infty}) \quad (17)$$

where T_g is defined as the temperature at which the dielectric relaxation time, τ_{α} , reaches an arbitrarily chosen long time of 10^2 s. The choice of 10^2 s for $\tau_{\alpha}(T_g)$ to define T_g is arbitrary. Other arbitrary long times can be chosen for $\tau_{\alpha}(T_g)$ to define T_g , and a more general expression for the ratio (E_{JG}/RT_g) is given by

$$E_{JG}/RT_g = 2.303[(1 - n)\log \tau_{\alpha}(T_g) - 11.7n - \log \tau_{\infty}] \quad (18)$$

The expression on the right-hand side of eq 17 or eq 18 gives a good account of the experimental value E_{JG}/RT_g for many neat glass-formers.³³ The ratio E_{JG}/RT_g is larger for smaller n and shorter τ_{∞} . It turns out that, for some neat glass-formers, the ones that have a larger n or small KWW exponent, $(1 - n)$

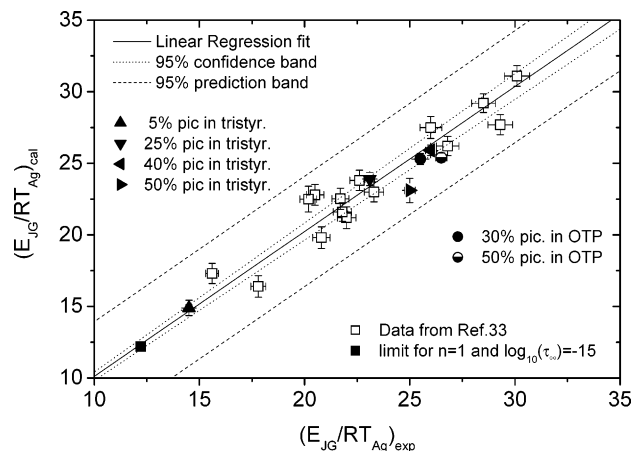


Figure 2. Comparison of the experimental and calculated ratio of the activation energy of the JG relaxation time, E_{JG} , to RT_{Ag} . The open squares represent data related to small molecular glass-formers from ref 33. The solid line shows the lower limit predicted by eq 19 for $\log(\tau_{\infty}) = -15$ in the limit of $\hat{n}_A \rightarrow 1$. The solid triangles and circles are related to the mixtures (in tri-styrene and OTP, respectively) analyzed in the present paper (derived from the same data shown in Figure 1). The solid line is a linear regression of reference data: $y = Bx$ and $B = 1.01 \pm 0.01$. The dotted and dashed lines mark the 95% confidence and prediction bands, respectively.

$\equiv \beta$, also have a shorter τ_{∞} for their JG β-relaxation. The compensating effects of n and τ_{∞} make it possible for the ratio, E_{JG}/RT_g , to be approximately constant for a number of neat glass-formers.

The analogue of eq 18 for component A in the mixtures $A_{1-x}B_x$ can be derived from eq 14 and is given by

$$E_{JG}/RT_{Ag} = 2.303[(1 - \hat{n}_A)\log \tau_{A\alpha,\max}(T_{Ag}) - 11.7\hat{n}_A - \log \tau_{\infty}] \quad (19)$$

where now T_{Ag} is the temperature at which the experimentally determined most probable α-relaxation time, $\tau_{A\alpha,\max}$, of component A assumes an arbitrarily chosen long time equal to $\tau_{A\alpha,\max}(T_{Ag})$. We now test the quantitative prediction of E_{JG}/RT_{Ag} given by eq 19 against the data of the α-relaxation and the JG β-relaxation of picoline in the mixtures with tri-styrene and with *o*-terphenyl.^{15,16} The experimental values of the prefactor τ_{∞} are taken from refs 15 and 16, and \hat{n}_A has previously been determined from the isothermal data and is given in Table 1 and Figure 1. The theoretical values of E_{JG}/RT_{Ag} calculated via eq 19, $(E_{JG}/RT_{Ag})_{\text{calcd}}$, are in good agreement with the experimental values, $(E_{JG}/RT_{Ag})_{\text{expt}}$, for the 2-picoline mixtures with tri-styrene or OTP (see Table 1). They are compared in Figure 2 together with the results of a number of neat glass-formers taken from ref 33.

Both the calculated and experimental values of the ratio $E_{JG}/(RT_{Ag})$ for the 25, 40, and 50% picoline mixtures are not far from the value 25, found for many neat glass-formers.^{33,66–68} One may notice from Table 1 for these three mixtures that the decrease of \hat{n}_A is accompanied by the increase of $\log \tau_{\infty}$. The near constancy of $E_{JG}/(RT_{Ag})$ arises from compensating changes of \hat{n}_A and τ_{∞} in eq 19. The 5% picoline mixture is an exception having a much smaller E_{JG}/RT_{Ag} equal to 14.5 from one estimate to 17.3 from another estimate.

(b) Non-Arrhenius Temperature Dependence of $\tau_{A,JG}$ at Temperatures above T_{Ag} . Like in neat glass-formers, the most probable α-relaxation time of component A in a binary mixture, $\tau_{A\alpha,\max}$, has non-Arrhenius temperature dependence at temperatures sufficiently high such that the α-dynamics of component

A are taking place in equilibrium. The non-Arrhenius temperature dependence is often approximately described by the Vogel–Fulcher–Tammann–Hesse (VFTH) equation

$$\tau_{A\alpha,\max}(T) = C \exp[D/(T - T_0)] \quad (20)$$

where C , D , and T_0 are constants. Upon cooling the mixture, $\tau_{A\alpha,\max}$ becomes long enough that the substructure of component A in the blend falls out of equilibrium at some temperature, T_{Ag} , the value of which depends on the cooling rate. At temperatures below T_{Ag} , the substructure is frozen and the temperature dependence of $\tau_{A\alpha,\max}$ is given by the Arrhenius equation

$$\tau_{A\alpha,\max}(T) = \tau_{A\alpha\infty} \exp(E_{A\alpha}/RT) \quad (21)$$

where $\tau_{A\alpha\infty}$ is the prefactor, $E_{A\alpha}$ the activation enthalpy, and R the gas constant. The coupling model relations, eqs 9 and 12 combined, lead immediately to the prediction of the corresponding temperature dependence of $\tau_{A,JG}$:

$$\tau_{A,JG} \approx \hat{\tau}_{A0} = (t_c)^{\hat{n}_A} (\tau_{A\alpha,\max})^{1-\hat{n}_A} = (t_c)^{\hat{n}_A} (C)^{1-\hat{n}_A} \exp\left[\frac{(1-\hat{n}_A)D}{T-T_0}\right], \quad T > T_{Ag} \quad (22)$$

and

$$\tau_{A,JG} \approx \hat{\tau}_{A0} = (t_c)^{\hat{n}_A} (\tau_{A\alpha,\max})^{1-\hat{n}_A} = (t_c)^{\hat{n}_A} (\tau_{A\alpha\infty})^{1-\hat{n}_A} \exp\left[\frac{(1-\hat{n}_A)E_{A\alpha}}{RT}\right], \quad T < T_{Ag} \quad (23)$$

From these, it is clear that the Arrhenius temperature dependence of $\tau_{A,JG}$ of component A at temperatures below T_{Ag} will give way to the VFTH dependence above T_{Ag} . The same prediction was made on neat glass-formers, which are eqs 22 and 23 after replacing \hat{n}_A therein by n_A . However, n_A of most neat small molecular glass-formers are less than 0.5. The distance between the α -relaxation and JG relaxation frequencies are not large enough to permit an unequivocal determination of τ_{JG} at temperatures above T_g . A case in point is neat sorbitol. Despite it having $n_A = 0.52$, some arbitrary fitting procedure^{69,70} has to be used to determine τ_{JG} at temperatures above T_g . Only by subjecting sorbitol to high pressure³¹ was it possible to determine τ_{JG} directly and show that the temperature dependence of τ_{JG} is in accord with eqs 22 and 23. In this respect, the study of the JG relaxation in mixtures, like picoline/tri-styrene, has an advantage. We have seen that \hat{n}_A of picoline can be increased significantly by increasing the content of the less mobile tri-styrene. The mixtures with 25 and 40% picoline have respectable large values of \hat{n}_A equal to 0.61 and 0.48, respectively (see Table 1). The JG loss peak is clearly observed at temperatures above and below T_{Ag} , from which $\tau_{A,JG}$ is directly determined. $\tau_{A,JG}$ indeed shows^{15,16} the change from the Arrhenius dependence of eq 23 to a stronger dependence at some temperature near T_{Ag} , consistent with eq 22. Hence, the dielectric data of the picoline component in the 25 and 40% picoline mixtures offer direct evidence that the Arrhenius temperature dependence of $\tau_{A,JG}$ in the glassy state does not continue to hold in the equilibrium liquid state. In mixtures with more than 40% picoline, the τ_{JG} 's were obtained by a fitting procedure^{15,16} that involves some assumption. Nevertheless, the deduced τ_{JG} 's also show the change of temperature dependence across T_{Ag} 's of the blends.

7. Conclusion

The coupling model has been applied to describe the α -relaxation dynamics of a component in binary mixtures of

two glass-formers. The strength of the coupling model in describing correctly the α -relaxation dynamics of a component in mixtures has been demonstrated in a recent paper⁷¹ and summarized in a recent review.⁷² The weakness of the model is the inability to use the experimental data to verify the expected and proposed change of the coupling parameter, \hat{n}_A , of component A upon mixing, the basic premise of the model. Unlike neat glass-formers, \hat{n}_A in mixtures cannot be determined directly from the frequency dispersion of the α -loss peak because of the broadening caused by concentration fluctuations. This is an undesirable situation because \hat{n}_A is the key parameter in the application of the coupling model to the α -relaxation dynamics of a component in binary mixtures. Somehow, we would like to determine \hat{n}_A from experiment, see how it changes upon mixing, and in the process verify or falsify the model. The present work comes to the rescue of this situation. By extending the coupling model further to consider the JG β -relaxation of a component and its relation to the α -relaxation of the same component in the mixture, we generate a relation between \hat{n}_A and the ratio of the α -relaxation time to the JG β -relaxation time. This new prediction enables us to obtain \hat{n}_A directly from the isothermal frequency spectrum of the mixture that shows both the α -relaxation and the JG β -relaxation of component A. We put this new prediction into practice by calculating \hat{n}_A of 2-picoline in binary mixtures with either tri-styrene or *o*-terphenyl from recently published broadband dielectric relaxation data of the α -relaxation and JG β -relaxation of 2-picoline. The results of \hat{n}_A obtained from experimental data show its change upon mixing is exactly the same as that assumed in previous works that address only the α -relaxation dynamics of a component in binary mixtures based on the coupling model.

The parallel description of the α -relaxation and the JG β -relaxation of a component in the mixture has other quantitative predictions on the JG β -relaxation time and its temperature dependence, and the relation of these quantities to the parameters of the α -relaxation of the same component. These predictions are also shown to be consistent with the data of 2-picoline in binary mixtures with either tri-styrene or *o*-terphenyl.

Acknowledgment. The research was supported at NRL by the Office of Naval Research, at the Università di Pisa by I.N.F.M., and by MIUR (Cofin2002).

References and Notes

- (1) Wetton, R. E.; MacKnight, W. J.; Fried, J. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 158.
- (2) Zetsche, A.; Kremer, F.; Jung, W.; Schulze, H. *Polymer* **1990**, *31*, 1883.
- (3) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 363.
- (4) Santangelo, P. G.; Roland, C. M.; Ngai, K. L.; Rizos, A. K.; Katerinopoulos, H. J. *J. Non-Cryst. Solids* **1994**, *172–174*, 1084.
- (5) Svanberg, C.; Bergman, R.; Jacobson, P.; Börjesson, L. *Phys. Rev. B* **2002**, *66*, 054304.
- (6) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.
- (7) Johari, G. P.; Power, G.; Vij, J. K. *J. Chem. Phys.* **2002**, *117*, 1714.
- (8) Johari, G. P. *J. Non-Cryst. Solids* **2002**, *307–310*, 317.
- (9) Shinyashiki, N.; Sudo, S.; Abe, W.; Yagihara, S. *J. Chem. Phys.* **1998**, *109*, 9843.
- (10) Sato, T.; Chiba, A.; Nozaki, R. *J. Mol. Liq.* **2002**, *101*, 99.
- (11) Sudo, S.; Shimomura, M.; Shinyashiki, N.; Yagihara, S. *J. Non-Cryst. Solids* **2002**, *307–310*, 356.
- (12) Nozaki, R.; Zenitani, H.; Minoguchi, A.; Kitai, K. *J. Non-Cryst. Solids* **2002**, *307–310*, 349.
- (13) Tyagi, M.; Murthy, S. S. N. *J. Phys. Chem. B*, submitted for publication, 2004.
- (14) Duvvuri K.; Richert, R. *J. Phys. Chem. B* **2004**, *108*, 10451.
- (15) Blochowicz, T.; Rössler, E. A. *Phys. Rev. Lett.* **2004**, *92*, 225701.
- (16) Blochowicz, T. *Broadband Dielectric Spectroscopy in Neat and Binary Molecular Glass Formers*; ISBN 3-8325-0320-X, Logos Verlag: Berlin, 2003.

- (17) Urakawa, O.; Fuse, Y.; Hori, H.; Tran-Cong, Q.; Adachi, K. *Polymer* **2001**, *42*, 765.
- (18) Kahle, S.; Korus, J.; Hempel, E.; Unger, R.; Höring, S.; Schröter, K.; Donth, E. *Macromolecules* **1997**, *30*, 7214.
- (19) Ngai, K. L. *Macromolecules* **1999**, *32*, 7140.
- (20) Zhang, Sh.; Jin, X.; Painter, P. C.; Runt, J. *Macromolecules* **2002**, *35*, 3636.
- (21) Ngai, K. L.; Paluch, M. *J. Chem. Phys.* **2004**, *120*, 875.
- (22) Ngai, K. L. *Comments Solid State Phys.* **1979**, *9*, 141.
- (23) Ngai, K. L.; Tsang, K. Y. *Phys. Rev. E* **1999**, *60*, 4511.
- (24) Ngai, K. L. *J. Phys.: Condens. Matter* **2003**, *15*, S1107.
- (25) Ngai, K. L.; Paluch, M. *J. Phys. Chem. B* **2003**, *107*, 6865.
- (26) Ngai, K. L.; Capaccioli, S. *J. Phys. Chem. B* **2004**, *108*, 11118.
- (27) Psurek, T.; Maslanka, S.; Paluch, M.; Nozaki, R.; Ngai, K. L. *Phys. Rev. E* **2004**, *70*, 011503.
- (28) Ngai, K. L.; Rendell, R. W. The Symmetric and Fully Distributed Solution to a Generalized Dining Philosophers Problem. In *Relaxation in Complex Systems and Related Topics*; Campbell, I. A., Giovannella, C., Eds.; NATO ASI Series 222; Plenum Press: New York, 1990; pp 309–316.
- (29) Schmidt-Rohr, K.; Spiess, H. W. *Phys. Rev. Lett.* **1991**, *66*, 3020.
- (30) Ngai, K. L. *J. Chem. Phys.* **1998**, *109*, 6982.
- (31) Paluch, M.; Roland, C. M.; Pawlus, S.; Ziolo, J.; Ngai, K. L. *Phys. Rev. Lett.* **2003**, *91*, 115701.
- (32) Prevosto, D.; Capaccioli, S.; Lucchesi, M.; Rolla, P. A.; Ngai, K. L. *J. Chem. Phys.* **2004**, *120*, 4808.
- (33) Ngai, K. L.; Capaccioli, S. *Phys. Rev. E* **2004**, *69*, 031501.
- (34) Böhmer, R.; Diezemann, G.; Hinze, G.; Rössler, E. *Prog. NMR Spectrosc.* **2001**, *39*, 191.
- (35) Hinze, G. *Phys. Rev. E* **1998**, *57*, 2010.
- (36) Vogel, M.; Rössler, E. *J. Chem. Phys.* **2000**, *114*, 5802.
- (37) Weeks, E. R.; Crocker, J. C.; Levitt, A.; Schofield, A.; Weitz, D. A. *Science* **2000**, *287*, 627.
- (38) Richert, R. *Europhys. Lett.* **2001**, *54*, 767. Duvvuri, K.; Richert, R. *J. Chem. Phys.* **2003**, *118*, 1356.
- (39) Böhmer, R.; Hinze, G.; Jörg, T.; Qui, F.; Sillescu, H. *J. Phys.: Condens. Matter* **2000**, *12*, A383.
- (40) Reinsberg, S. A.; Heuer, A.; Doliwa, B.; Zimmermann, H.; Spiess, H. W. *J. Non-Cryst. Solids* **2002**, *307–310*, 208.
- (41) Ngai, K. L.; Lunkenheimer, P.; León, C.; Schneider, U.; Brand, R.; Loidl, A. *J. Chem. Phys.* **2001**, *115*, 1405.
- (42) Schneider, U.; Brand, R.; Lunkenheimer, P.; Loidl, A. *Phys. Rev. Lett.* **2000**, *84*, 5560.
- (43) Casalini, R.; Roland, C. M. *Phys. Rev. B* **2004**, *69*, 094202.
- (44) Barton, A. F. M. *Handbook of solubility parameters and other cohesion parameters*; CRC Press: Boca Raton, FL, 1982. Barton, A. F. M. *Chem. Rev.* **1975**, *75*, 731. Van Krevelen, D. W. *Properties of Polymers*; Elsevier Publ.: Amsterdam (NL), 1997.
- (45) Miller, J. B.; McGrath, K. J.; Roland, C. M.; Trask, C. A.; Garroway, A. N. *Macromolecules* **1990**, *23*, 4543.
- (46) Chung, G.-C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1994**, *27*, 5729.
- (47) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261.
- (48) Roland, C. M.; Ngai, K. L. *J. Rheol.* **1992**, *36*, 1691.
- (49) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 363; **2000**, *33*, 3184.
- (50) Alegria, A.; Colmenero, J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 4486.
- (51) Roland, C. M.; Ngai, K. L. *Macromolecules* **1995**, *28*, 4033.
- (52) Roland, C. M.; Ngai, K. L.; O'Reilly, J. M.; Sedita, J. S. *Macromolecules* **1992**, *25*, 3906.
- (53) Ngai, K. L. *J. Phys. Chem. B* **1999**, *103*, 10684–10694.
- (54) Bohmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *J. Chem. Phys.* **1993**, *99*, 4201.
- (55) Ngai, K. L. *J. Chem. Phys.* **1998**, *109*, 6982.
- (56) Hensel-Bielowka, S.; Paluch, M.; Ziolo, J.; Roland, C. M. *J. Phys. Chem. B* **2002**, *106*, 12459.
- (57) Lunkenheimer, P.; Schneider, U.; Brand, R.; Loidl, A. *Contemp. Phys.* **2000**, *41*, 15.
- (58) Duvvuri, K.; Richert, R. *J. Chem. Phys.* **2003**, *118*, 1356.
- (59) León, C.; Ngai, K. L.; Roland, C. M. *J. Chem. Phys.* **1999**, *110*, 11585.
- (60) Paluch, M.; Ngai, K. L.; Hensel-Bielowka, S. *J. Chem. Phys.* **2001**, *114*, 10872.
- (61) Chung, S. H.; Johari, G. P.; Pathmanathan, K. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2655.
- (62) Svanberg, C.; Bergman, R.; Jacobson, P. *Europhys. Lett.* **2003**, *64*, 358.
- (63) Casalini, R.; Roland, C. M. *Phys. Rev. Lett.* **2003**, *91*, 015702.
- (64) Roland, C. M.; Casalini, R.; Paluch, M. *Chem. Phys. Lett.* **2003**, *367*, 259.
- (65) Blochowicz, T.; Tschirwitz, C.; Benkhof, S.; Rössler, E. *J. Chem. Phys.* **2003**, *118*, 7544.
- (66) Kudlik, A.; Tschirwitz, C.; Benkhof, S.; Blochowicz, T.; Rössler, E. *Europhys. Lett.* **1997**, *40*, 649.
- (67) Kudlik, A.; Tschirwitz, C.; Blochowicz, T.; Benkhof, S.; Rössler, E. *J. Non-Cryst. Solids* **1998**, *235–237*, 406.
- (68) Kudlik, A.; Benkhof, S.; Blochowicz, T.; Tschirwitz, C.; Rössler, E. *J. Mol. Struct.* **1999**, *479*, 210.
- (69) Fujima, T.; Frusawa, H.; Ito, K. *Phys. Rev. E* **2002**, *66*, 031503.
- (70) Nozaki, R.; Suzuki, D.; Ozawa, S.; Shiozaki, Y. *J. Non-Cryst. Solids* **2002**, *235–237*, 393.
- (71) Ngai, K. L.; Roland, C. M. *Macromolecules* **2004**, *37*, 2817.
- (72) Ngai, K. L.; Roland, C. M. *Rubber Chem. Technol. Rubber Rev.* **2004**, *77*, 579.