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Dielectric relaxation processes in solid and supercooled liquid solutions of acetaminophen and nifedipine

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Abstract

Dielectric spectroscopy was used to study supercooled liquid and glassy mixtures of acetaminophen and nifedipine. The glass transition temperature T_g was found to vary continuously as a function of the acetaminophen concentration x , indicating complete miscibility of these drugs. The steepness index m characterizing the α -relaxation as well as the dispersion width of this process were almost independent of x . A weak Johari–Goldstein β -relaxation was identified by its typical decoupling from the α -process. A well-resolved low-temperature γ -relaxation was found and ascribed to a side group motion, predominantly of the nifedipine molecule. The energy barriers hindering this motion exhibit a wide distribution, with a mean value of typically about 3500 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Amorphous drugs and pharmaceutical alloys are typically characterized by a free energy that is higher than that of their crystalline counterparts. Therefore, many vitreous medicaments exhibit an increased dissolution in the body and hence a better therapeutic activity. Recently, the glass transition, several relaxation phenomena and the crystallization kinetics of non-crystalline drugs were studied by a number of researchers under non-physiological conditions. One motivation for such investigations is to understand the parameters affecting the production and processing of amorphous medicaments better. Another motivation is that the crystalline substances often exhibit several phases, and a particular crystalline modification may be difficult to obtain or hard to isolate in pure form [1]. Among the well-documented examples for such a polymorphism are indomethacin [2], nifedipine (NIF) [3] and acetaminophen (ACE) [4, 5]. However, sufficiently fast quenching can lead to a well-defined, albeit amorphous state. Of course, there are many routes into the glassy state [6]. Among them mechanical milling is particularly promising in the pharmaceutical field [7]. This is because high temperatures can be avoided, which is an issue for some thermally unstable substances.

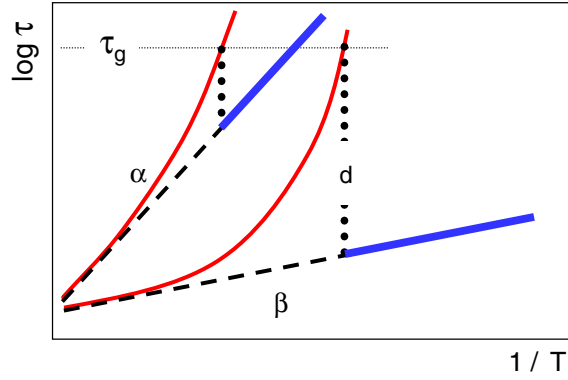


Figure 1. Sketch showing that the degree d of tangential decoupling in supercooled liquids depends on the bending of the α -relaxation curve and hence on the steepness of $\tau(T)$ near T_g at which the relaxation time is defined to be $\tau_g = 100$ s. With the high-temperature limit τ_0 , the minimum fragility is $m_{\min} = \log_{10}(\tau_g/\tau_0)$. See figure 2.8 in [21]. The dashed lines are meant to indicate that the β -process may deviate from an Arrhenius behaviour for $T > T_g$.

The calcium channel blocker NIF and the antipyretic ACE, which are the focus of the present article, are, however, stable to somewhat above their melting points of $T_m = 446$ and 443 K [8, 9], respectively. Thus, the supercooled liquid state of the pure substances is relatively easy to access by quenching from the melt and it has been studied before by various methods. These include calorimetry [10–14], proton nuclear magnetic resonance (NMR) [8] and dielectric spectroscopy [15, 16]. Previously we reported on dielectric measurements of an equimolar mixture of NIF and ACE, i.e. $\text{NIF}_{1-x}\text{ACE}_x$ with $x = 0.5$ [17], also including the relaxation processes occurring below the glass transition temperature T_g . Apart from the Johari–Goldstein (JG) β -process which is quasi-universally found in supercooled liquids [18], an additional process, a so-called γ -relaxation, was identified in the $x = 0.5$ sample. In the present article we extend the dielectric experiments to cover the whole range of ACE concentrations, x .

To avoid crystallization is a concern for practical considerations of amorphous pharmaceuticals. In this respect it is important to note that secondary relaxations were reported to have an impact on the crystallization kinetics [10, 19]. One way to characterize the β -, γ -, etc relaxations, that below the bifurcation temperature are decoupled from the primary relaxation, is via the decoupling index [20]

$$d_{\beta,\gamma} = \log_{10} \left(\frac{\tau_\alpha}{\tau_{\beta,\gamma}} \right) \Big|_{T=T_g}. \quad (1)$$

$d_{\beta,\gamma}$ counts the number of decades separating the β - or γ -relaxation from the primary process. The relation of $d_{\beta,\gamma}$ to various other metrics of decoupling of relaxation times τ was discussed in [17]. As suggested some time ago [21], the degree of decoupling can be related with the curvature of the α -relaxation trace and hence the steepness of $\tau_\alpha(T)$ as measured via the index [22]

$$m(T_g) = \frac{d \log_{10}(\tau_\alpha/s)}{d(T_g/T)} \Big|_{T=T_g}. \quad (2)$$

Typical values for m range from $m_{\min} = 16 \dots 17$ to $m_{\max} \approx 170$ [23]. Let us assume a tangential decoupling as illustrated in figure 1 and a thermally activated, decoupled relaxation

which at least for $T < T_g$ follows an Arrhenius law,

$$\tau_{\beta,\gamma} = \tau_{0,\beta,\gamma} \exp(E_{\beta,\gamma}/T), \quad (3)$$

with an energy barrier $E_{\beta,\gamma}$. It should be emphasized that the Arrhenius dependence may break down above T_g , where more complex behaviours have sometimes been reported [24, 25]. This is the reason why in figure 1 the β -traces are represented as dashed lines. However, in order to define an Arrhenius law only two points are required, e.g. the relaxation time $\tau_{0,\beta,\gamma}$ (corresponding to $T \rightarrow \infty$) and $\tau_{\beta,\gamma}$ at T_g obtained from equation (1). Combining equations (1)–(3) one finds

$$\frac{E_{\beta,\gamma}}{T_g} = \frac{m_{\min} - d_{\beta,\gamma}}{\log_{10}(e)} \quad \text{or} \quad d_{\beta,\gamma} = m_{\min} - \frac{E_{\beta,\gamma}}{T_g \ln(10)}. \quad (4)$$

Kudlik *et al* showed for a number of glass formers that the ratio E_{β}/T_g is near 24, although smaller values were also reported [26]. Taking $E_{\beta}/T_g = 24$, equation (4) yields $d_{\beta} \approx 6$ decades. Ngai quantified the relationship between the decoupling and the non-exponentiality of the primary relaxation [27], which for many glass formers is in turn related to the steepness index m [22]. This prompted Ngai and co-workers to suggest a criterion for the distinction of JG-type from non-JG relaxations [28]. For the latter relaxations side group motions provide an example.

2. Experimental details

Nifedipine ($C_{17}H_{18}N_2O_6$) and acetaminophen ($C_8H_9NO_2$) with nominal purities of $\geq 98\%$ were used. Details of the experimental methods and of the sample preparation were described in [17]. For the present work the acetaminophen compositions $x = 0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875$ and 1 were prepared, and usually two runs were performed for each x . In order to avoid any ambiguity arising from a possible not entirely complete filling of the capacitor, the dielectric permittivity and the dielectric loss are presented in normalized form as $\varepsilon'_n = \varepsilon'/\varepsilon'(T_{\text{ref}})$ and $\varepsilon''_n = \varepsilon''/\varepsilon''(T_{\text{ref}})$, respectively. We choose $T_{\text{ref}} \approx 120$ K, which is close to the low-temperature limit of our set-up, with $\varepsilon'(T_{\text{ref}})$ typically being in the range 2 . . . 2.7.

3. Results and analysis

3.1. Structural relaxation

As a characteristic example in figure 2 we present $\varepsilon'_n(\omega)$ and $\varepsilon''_n(\omega)$ for NIF_{0.25}ACE_{0.75} covering the temperature range in which the α -relaxation can be measured at audio frequencies. Well-defined dispersions and dielectric loss peaks show up. The data were fitted using a Havriliak–Negami expression [29]

$$\varepsilon^*(\omega) = \varepsilon'(v) - i\varepsilon''(v) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1 + (2\pi i v \tau)^{\alpha}]^{\beta}} + \frac{i\sigma_0}{2\pi v \varepsilon_0} \quad (5)$$

where a conductivity term was added. The high-frequency dielectric constant, the dispersion step and the electrical dc conductivity are denoted as ε_{∞} , $\Delta\varepsilon$ and σ_0 , respectively. The parameters $0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$ determine the slopes of $\varepsilon''(\omega)$ in a double logarithmic plot. For $\alpha \neq 1$ and $\beta = 1$, equation (5) reduces to the Cole–Cole form, and for $\beta \neq 1$ and $\alpha = 1$ the Cole–Davidson form is recovered [30]. As figure 2 demonstrates, equation (5) fits the data for $x = 0.75$ very well. Similarly good agreement was also obtained for $x = 0.5$ [17] and for the other compositions studied in the present work (not shown). In all fits it turned out that $\alpha = 1$, and for the samples with $x < 1$ the parameter $\beta = 0.54 \pm 0.04$ was

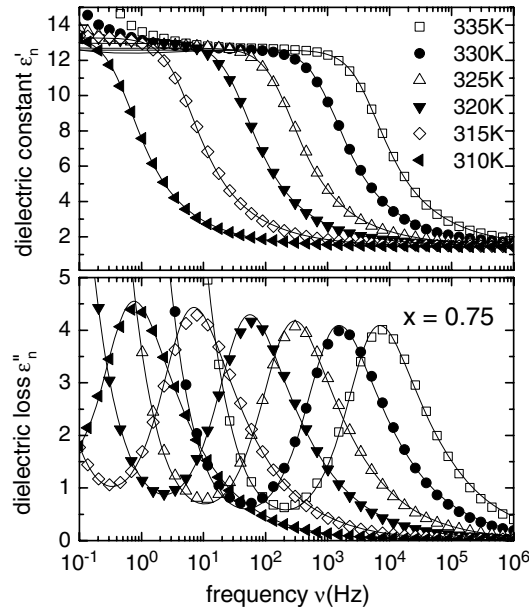


Figure 2. (a) Normalized dielectric constant and (b) normalized dielectric loss of $\text{NIF}_{0.25}\text{ACE}_{0.75}$. The solid lines are fits using equation (5).

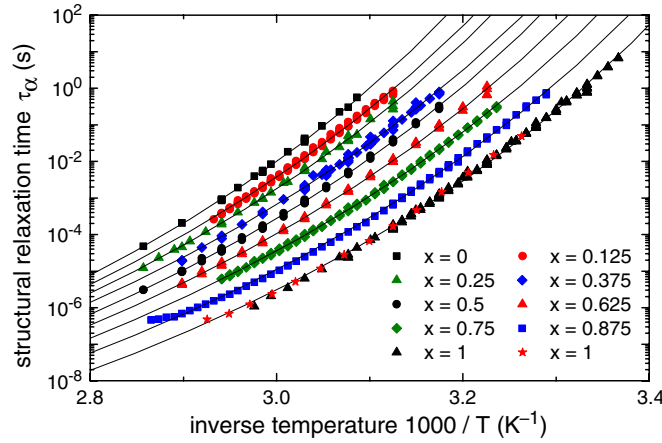


Figure 3. Arrhenius plot of the α -relaxation times for $\text{NIF}_{1-x}\text{ACE}_x$ from this work. The data marked with the asterisks are from [15]. The solid lines are fits using equation (6) and the parameters given in table 1.

found to be independent of temperature within the experimental error. For $x = 1$ we find $\beta = 0.64 \pm 0.01$, corresponding to a Kohlrausch exponent $\beta_K = 0.75$.¹ This agrees with results from calorimetry [10], and is only slightly smaller than that from a previous dielectric measurement [15].

The relaxation times τ obtained from the fits are plotted in figure 3. As the solid lines in this figure show, they can be described well using the Vogel–Fulcher equation

¹ Reference [31] gives $\beta_K = 0.97\beta + 0.144$ for $0.2 \leq \beta \leq 0.6$ and $\beta_K = 0.683\beta + 0.316$ for $0.6 \leq \beta \leq 1.0$.

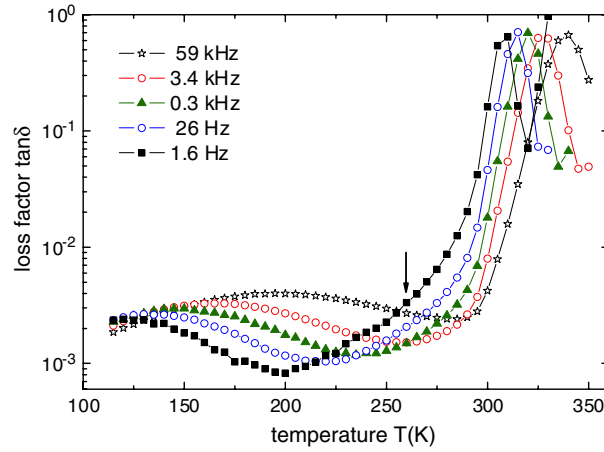


Figure 4. Loss factor of $\text{NIF}_{0.25}\text{ACE}_{0.75}$. The lines are drawn to guide the eye. The arrow marks the JG loss peak temperature expected on the basis of equation (7).

Table 1. Parameters describing the α -relaxation times of $\text{NIF}_{1-x}\text{ACE}_x$ using equation (6).

x	0	0.125	0.25	0.375	0.5	0.625	0.75	0.875	1
B (K)	3129	3148	3108	3141	3025	2990	2912	2811	2757
T_0 (K)	242	239	238	234	235	233	232	231	230

$$\tau_\alpha = \tau_{0,\alpha} \exp\left(\frac{B}{T - T_0}\right), \quad (6)$$

where T_0 and B are empirical parameters. Their composition dependence is given in table 1. One recognizes that T_0 is only slightly dependent on x , while B exhibits major variations. The pre-exponential factor could be kept constant, $\tau_{0,\alpha} = 10^{-17}$ s, for all compositions.

With the data in table 1 or figure 3 one obtains that the glass transition temperatures defined as $T_g = T_g(\tau_\alpha = 100 \text{ s})$ vary linearly with x . This behaviour demonstrates the good miscibility of the two drugs. We find $T_g = 314.1 \text{ K}$ for $x = 0$ and $T_g = 293.2 \text{ K}$ for $x = 1$. These values are somewhat lower than the corresponding onset temperatures $T_{g,\text{cal}} = 322 \text{ K}$ [8] and $T_{g,\text{cal}} = 296.4 \text{ K}$ [32] from calorimetry. On the basis of equation (2), the steepness index was also calculated, and $m = 83 \pm 2$ for $x \neq 1$ and $m = 90$ for $x = 1$ were found.

3.2. Low-temperature processes

For temperatures below T_g , signatures for two additional relaxation processes were detected for $\text{NIF}_{1-x}\text{ACE}_x$. The maximum dielectric losses associated with these relaxations are more than two orders of magnitude weaker than those of the α -process. As an example, in figure 4 we show the loss factor $\tan \delta = \varepsilon''/\varepsilon'$ of $\text{NIF}_{0.25}\text{ACE}_{0.75}$ ($T_g = 300 \text{ K}$) for several frequencies. At temperatures $T < 200 \text{ K}$ the loss peaks are clearly resolved which, in analogy to $x = 0.5$ [17], can be ascribed to an intramolecular relaxation. In figure 4 the JG relaxation is visible at the lowest frequencies, but only as a shoulder. Its estimated position for a measuring frequency of $\nu = 1.6 \text{ Hz}$ is marked by an arrow. Its temperature position is calculated from

$$T = \frac{-24T_g}{\ln(2\pi\nu\tau_{0,\beta})} \quad (7)$$

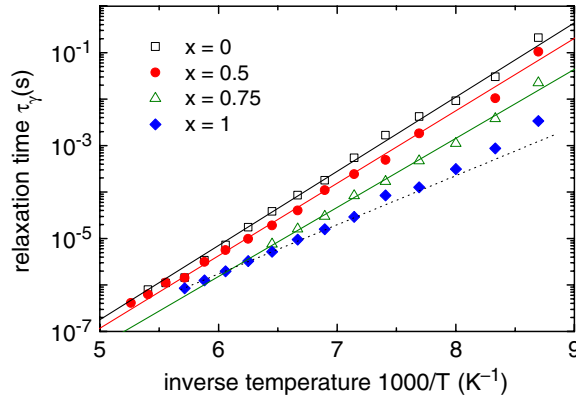


Figure 5. Arrhenius plot of the relaxation times τ_γ as obtained from the Cole–Cole fits described in the text. The lines are fits using equation (3). The dotted line corresponds to an energy barrier of 2500 K.

where a prefactor of $\tau_{0,\beta} = 10^{-14}$ s is used. Equation (7) follows from equation (3) for $E_\beta/T_g = 24$. The increase in $\tan \delta$ seen for $T > 310$ K at low frequencies is due to the mobility of impurity ions.

For an initial characterization of the γ -process one can determine the loss maxima from figure 4. However, in order to analyse this process in more detail it is useful to fit the data in the $\varepsilon''(\omega)$ representation. Frequency-dependent dielectric data were already presented in [17] for $x = 0$ and 0.5, and since the data for the other concentrations look qualitatively similar, they are not reproduced here. These data could all be fitted well using the Cole–Cole expression, equation (5), with $\beta = 1$ (not shown). The time constants resulting from these fits are plotted in figure 5 for four concentrations. For $0 \leq x \leq 0.5$ they almost coincide, while, at a given temperature, those for larger $x < 1$ are somewhat shorter. The relaxation times for $x < 1$ follow a thermally activated behaviour, equation (3), with $\tau_{0,\gamma} = 5.8 \times 10^{-14}$ s, independent of x . The energy barriers E_γ are in the range of about 3600 to about 3300 K; see below. For pure ACE, slight deviations from an Arrhenius law are seen in figure 5.

The temperature dependence of the width parameter α resulting from the fits to the γ -relaxation peaks is shown in figure 6. For $x \leq 0.875$ the width parameters almost agree. The full half-widths W of the corresponding distribution of correlation times, estimated from these α -values according to [33]

$$W = \frac{2 \operatorname{arccosh}\{2 + \sin[\pi(1 - \alpha)/2]\}}{\alpha \ln(10)} \quad (8)$$

are in the range from 7 to 14 decades. Thus they are much larger than expected for a JG process. The strong increase in W with decreasing temperature is compatible with a T^{-1} behaviour. Such an evolution of the broadening is expected if relaxation occurs in the presence of a Gaussian distribution of energy barriers,

$$G(E) = \frac{1}{\sigma_E \sqrt{2\pi}} \exp\left[-\frac{(E - E_\gamma)^2}{2\sigma_E^2}\right], \quad (9)$$

provided its variance $\sigma_E = W/(1.023T)$ [34] is (at least almost) temperature independent. Using the data for $x < 1$ one obtains $\sigma_E \approx 1500$ K, so the corresponding full half-width of $G(E)$ is $\Sigma \approx 2.35\sigma_E$, which is comparable to E_γ . Figure 6 reveals that at high temperatures the width parameter for the γ -process of ACE evolves somewhat differently from that of the samples with $x < 1$.

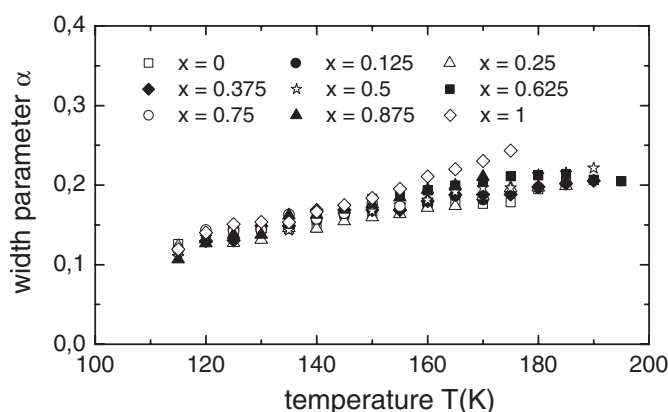


Figure 6. Width parameter α as a function of temperature for all concentrations investigated in the present work. Note the somewhat larger values of α for pure ACE at $T > 150$ K.

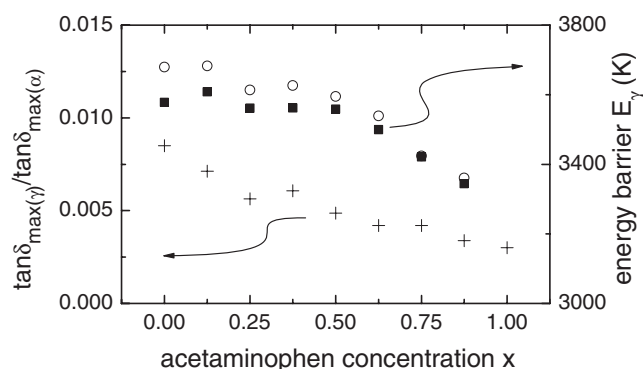


Figure 7. Parameters characterizing the γ -process. The left-hand scale shows the ratio of the loss peak maxima of the γ - to that of the α -process. The ratio was determined at a measuring frequency of 677 Hz. The right-hand scale refers to the energy barriers of the γ -process. The relaxation times were obtained from the fits described in the text (open symbols) or from the maxima of $\tan \delta$ (closed symbols).

4. Discussion and conclusions

For $\text{NIF}_{1-x}\text{ACE}_x$, the magnitude of the decoupling index d_γ , which we determined to be 11 ± 1 independent of composition, signals that the low-temperature loss peaks are due to a non-JG relaxation. An unambiguous assignment of the side group motion responsible for this γ -process is not possible using dielectric measurements alone. Here NMR experiments, for example of the type recently performed for amorphous acetyl salicylic acid [35], may be helpful. However, indirect information concerning the nature of the γ -process can be obtained from the concentration dependence of the relative strength of the corresponding dielectric loss peaks, which are shown in figure 7.

Here we plot the ratio of the maxima of the γ - to those of the α -peaks. When going from $x = 0$ to $x = 1$ it is seen that this ratio drops to about one third of its value for pure NIF. Concomitantly the maximum α -amplitude increases by only about 50%. These observations strongly suggest that it is predominantly a side group motion of NIF which is responsible for the γ -process. The observation that the amplitudes of the loss peaks are smallest for pure

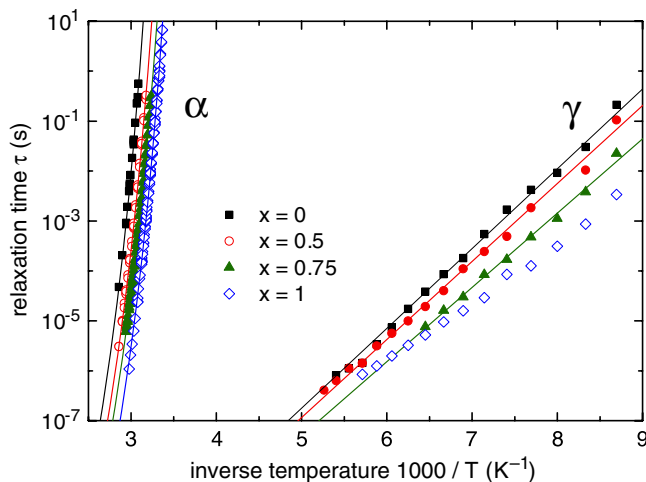


Figure 8. Relaxation map of $\text{NIF}_{1-x}\text{ACE}_x$ showing the α - and γ -relaxation times for selected compositions.

ACE implies that other relaxation processes, if they exist, will have the largest impact on the dielectric loss of that substance. The deviations from the Arrhenius law seen in figure 5 indeed suggest that very weak additional background contributions are present for ACE. *Nearly* constant loss phenomena, observed for a number of glasses, are thus a possible candidate to account for the behaviour seen in ACE. High-resolution dielectric measurements at low temperatures, such as those reported, for example, in [36, 37], could help to clarify this issue.

While the parameters characterizing the α -relaxation times vary significantly with composition, for $x < 1$ the energy barriers of the γ -process change by about 10% at most; see figure 7. The difference in E_γ arising from the method of determination is less than 3%. For $x \leq 0.5$ we find that E_γ is practically independent of the composition, and only for larger x does it decrease slightly. This almost absent sensitivity to x and hence to the detailed structure of the local environment of the relaxing side groups demonstrates that the γ -process is predominantly intramolecular in nature.

The JG β -process is very weak for all $\text{NIF}_{1-x}\text{ACE}_x$ alloys, and is only recognized from a shoulder in $\tan \delta$; see figure 4. This precludes more detailed analyses of this process. To gain an overview of the relaxation times obtained for the α - and γ -relaxations, we summarize them in figure 8 for several concentrations x .

The α -relaxation times plotted in figures 3 and 8 illustrate the finding that, while T_g shows a pronounced variation with composition, the steepness as measured by $m = 83 \dots 90$ is only weakly affected by changes in x . Furthermore, the $\text{NIF}_{1-x}\text{ACE}_x$ alloys exhibit a somewhat larger steepness index than other drugs such as indomethacin ($m = 79$) [2], aspirin ($m = 79$) [35] or nicotine ($m = 65$) [38].

To summarize, we find that NIF and ACE, which show almost identical melting temperatures, are fully miscible in their liquid and glassy states. Three relaxation processes, i.e. an α -, a JG β - and an intramolecular γ -process, are identified by dielectric measurements of the $\text{NIF}_{1-x}\text{ACE}_x$ alloys covering the whole range of concentrations, x . The spectral widths of the α - and γ -processes are almost independent of composition, except for ACE, which exhibits somewhat narrower spectra. The Kohlrausch exponent $\beta_K = 0.67$ estimated for $x < 1$ indicates a relatively narrow distribution of α -relaxation times. For the γ -process, on the other hand, the width of the distribution of energy barriers, which is responsible for the temperature-dependent

broadening of $\varepsilon''(\omega)$, is comparable to its mean E_γ . The energy barriers are about 3600 K for $x \leq 0.5$ and drop to below 3400 K as the NIF content further decreases.

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