Non-exponential and linear characters of the irreversible enthalpy relaxation functions in dibenzofuran - fluorene solid solution systems and their interpretation

Non-exponential and linear characters of the irreversible enthalpy relaxation functions in dibenzofuran–fluorene solid solution systems and their interpretation

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Abstract. Heat capacities and spontaneous heat evolution/absorption effects in solid solution systems between dibenzofuran and fluorene were measured with an adiabatic calorimeter. Glass transitions due to freezing-in of the reorientational motion of molecules in the stable crystalline state were observed throughout the composition range. The enthalpy relaxation processes associated with the transition were precisely tracked around 300 K by the temperature jump method under adiabatic conditions. The processes exhibited a non-exponential character and the non-exponentiality characterized by the β parameter of a stretched exponential function was found to increase as the sample became impure with doping of the second component into the pure substance. The relaxation function was, meanwhile, found to show a linearity against the magnitude of the temperature jump. Both the non-exponential and the linear characters were interpreted on the basis of computer simulation experiments as being due to the presence of the distribution of activation energies for the reorientation of molecules.

1. Introduction

The equilibrium configuration of molecules in the condensed state changes as a function of temperature. The configurational change generally proceeds as each molecule alters its position or orientation by surmounting some potential barrier. Thus, the characteristic time for the change becomes long at low temperatures, resulting in the freezing-in of the configuration of molecules when the time becomes longer than the experimental time scale of 10^2–10^6 s [1, 2]. This freezing-in phenomenon is called a glass transition and, in the transition region, the relaxation phenomenon of thermodynamic quantities, such as enthalpy and volume, is observed as the configuration relaxes from non-equilibrium to equilibrium state [3, 4]. The glass transitions have been found in supercooled liquid, supercooled plastically crystalline, supercooled liquid crystalline and even stable crystalline phases [1, 5]. Molecules in the glassy liquid are frozen in the disordered arrangement with respect both to the positional and to the orientational degrees of freedom. On the other hand, molecules in the stable crystalline phase, being essentially in the configurationally ordered state, are allowed to be only partially disordered concerning either of the two degrees and the glassy state is realized when the partial disorder is frozen kinetically.

Quite a contrast has been found between the relaxation properties of liquids and those of stable crystals for pure substances [6, 7]. In the former case, the average relaxation times exhibit a non-Arrhénius temperature-dependence, the enthalpy relaxation follows a non-exponential function and the functions show a remarkable nonlinearity against the magnitude

of the temperature jump taken just before the relaxation measurement. In the latter stable crystals of pure substances, on the other hand, the relaxation follows an exponential form and its characteristic times exhibit an Arrhénius behaviour. We have previously indicated that the nonlinearity of the relaxation function in glassy liquids would be mainly attributed to the non-Arrhénius properties of relaxation times [8, 9]. If this is correct, the relaxation in the crystalline state even for solid solutions should exhibit a linearity against the magnitude of the jump. Table 1 summarizes the characteristic points of the properties. The above differences would reflect the following structural characters. Molecules in liquid, as stated above, are essentially in the disordered state both in the positional and in the orientational degrees of freedom, and there exist only short-range, and often medium-range, structurally 'ordered regions' in the configuration of molecules. So-called 'structured clusters' appear and disappear within the time duration of the so-called fluctuation of the liquid structure. The average size of these clusters is considered to increase gradually with decreasing temperature and also to change gradually with time evolution after a sudden temperature jump. As a matter of course, there exists some distribution in the energetic circumstances of molecules in correspondence to the presence of structural fluctuation. In the stable crystalline state, on the other hand, only partial disorders, if there are any remaining, are arrested below the glass transition temperature. The structure of the molecular arrangement and therefore the energetic parameters for the molecular rearrangement are expected not to change very much with temperature or with time after some sudden temperature jump; so especially in pure substances, there would be essentially no distribution in the parameters.

Table 1. Comparative structural characters and relaxation properties of glasses in the liquid state and in the stable crystalline state with a small fraction of configurational disorder remaining.

| | Liquid phase | Stable crystalline phase | |
		Solid solution	Pure substance
Temperature-dependence of molecular arrangement structure	Present	Absent	Absent
Microscopic structure in molecular arrangement	Heterogeneous	Heterogeneous	Homogeneous
Temperature-dependence of average relaxation times	Non-Arrhénius	Arrhénius	Arrhénius
Relaxation function	Non-exponential Nonlinear	(Non-exponential?) (Linear?)	Exponential Linear

A solid solution is a crystal in which two or more different components are homogeneously mixed on the mesoscopic scale [10]. Structural characters of solid solutions are in between those of liquids and crystals of pure substances. The structural arrangement of molecules and therefore the potential curve for the rearrangement of each molecule do not change very much with temperature or with the progress of relaxation processes just as in crystals of pure substances and in 'strong' liquids [6]. However, the microscopic structure concerning the molecular arrangement is slightly different from place to place according to the difference in the species of rearranging molecule and in the molecules surrounding it. The activation energies for the molecular rearrangement, for example, are then expected to have some distribution depending on the molecular composition. This character is rather similar to that in liquids, though the distribution in liquids is due to the different structural circumstances of each molecule. In such structural situations of

solid solutions, their relaxation functions are expected to be non-exponential and linear with respect to the magnitude of the temperature jump, differently from those either of 'fragile' liquids or of pure glassy crystals, and must be suggestive of a clarification of the complicated properties of the liquids.

On the basis of the above views on the structural characters and relaxation properties, we investigated the enthalpy relaxations in the solid solutions consisting of two polycyclic pseudo-planar molecules, dibenzofuran and fluorene. Both crystals are known to exhibit glass transitions due to freezing-in of a small fraction of remaining orientational disorder [11] and to form a complete solid-solution system between themselves [12]. The relaxation processes were experimentally tracked under adiabatic conditions and characterized by fitting a stretched exponential function to the data. The processes were also computer-simulated under the assumption that the energetic circumstance for reorientation of each molecule did not change with the temperature and the degree of ordering, and were compared with the experimental results of the above solid solutions and the previous ones of liquids [8, 9].

2. Experimental

Commercial dibenzofuran and fluorene reagents, purchased from Tokyo Kasei Kogyo Co Ltd, were purified by recrystallization from ethanol three times and n-hexane once and by subsequent vacuum sublimation. The purities of the batches of refined dibenzofuran and fluorene samples were determined by the calorimetric fractional-melting method as described elsewhere to be 0.9993 and 0.9971, respectively [11]. The respective refined samples were loaded into a calorimeter cell with helium gas at 0.1 MPa [13]. The binary mixtures between the two compounds, $(C_{12}H_8O)_{1-x}(C_{13}H_{10})_x$, were prepared by melting the two refined pure samples within the cell. Each mixture was kept at above its melting point until a melt homogeneous in composition had been attained. Then the cell was kept at a temperature only a little lower than the melting point for a long enough time to achieve a homogeneous solid solution. The composition was determined by the gravitational method. The masses of the sample used were weighed to be 16.639 g for $x = 0$, 16.748 g for $x = 0.0066$, 17.048 g for $x = 0.0243$, 18.468 g for $x = 0.1001$, 18.608 g for $x = 0.8501$ and 15.911 g for $x = 1$, respectively.

Heat capacity measurements were carried out by an intermittent heating method with an adiabatic calorimeter described previously [13]. The initial temperature (T_i) of the cell was followed for 10 min in the temperature rating period, some known quantity of electrical energy (ΔE) was supplied to the cell and then the final temperature (T_f) was followed again for 10 min; the gross heat capacity (C) was evaluated to be $C = \Delta E/(T_f - T_i)$ at $T_{av} = (T_f + T_i)/2$. The latter temperature rating served as the former rating in the next set of heat capacity measurement. A platinum resistance thermometer calibrated on the ITS-90 temperature scale was used; the imprecision of the thermometry was found to be within 10^{-5} K [13]. The inaccuracy and imprecision of the heat capacity obtained were estimated previously to be less than ± 0.3 and $\pm 0.06\%$, respectively [13].

Tracking of the enthalpy relaxation process was carried out by the temperature jump method [14] under adiabatic conditions, according to the procedure illustrated in figure 1. The line from the upper right-hand side to the lower left-hand side in figure 1 represents the equilibrium configurational enthalpy as a function of temperature in the glass transition region. The calorimeter cell was first held for a long enough time to reach equilibrium at T_i, then the temperature was suddenly made to jump from T_i to T_a by $\Delta_j T (= T_a - T_i)$, and the temperature of the cell was tracked for a long time. The tracking temperature (T_a) was chosen to be the temperature at which the relaxation time became about 5 ks. It has
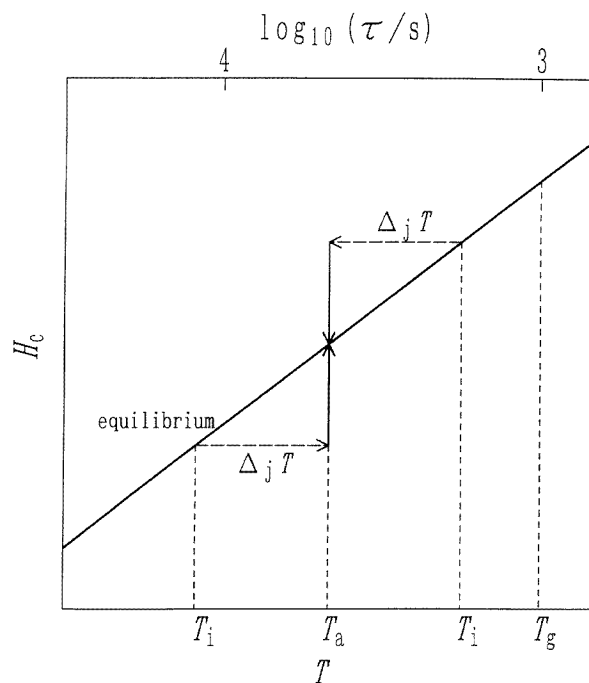
Figure 1. A schematic diagram illustrating the temperature jump method for the configurational enthalpy versus temperature (or relaxation time) relation in a glass transition temperature region. A thick full curve represents the configurational enthalpy under equilibrium. T_g, T_i and T_a denote the glass transition temperature, the temperature at which the sample is annealed for a long time before the jump and the temperature at which the enthalpy relaxation is tracked for a long time, respectively; the magnitude of the temperature jump is defined by $\Delta_j T = T_a - T_i$.

been pointed out that the tracking of the enthalpy relaxation in a glassy liquid should be executed under constant temperature conditions [15]. However, the configurational degrees of freedom responsible for the glass transition in the stable crystalline phase are generally very small compared with those in the supercooled liquid phase and thus the magnitude of the temperature change due to the enthalpy relaxation is quite small in a crystal; for instance, in the case of dibenzofuran, the magnitude is only about 60 mK when the temperature jump is taken to be ± 3 K. The influence of the temperature change on the relaxation function is negligible within the errors of the parameters derived. On account of the situation, the enthalpy relaxation ($\Delta H_c(t)$) was tracked under adiabatic conditions and was monitored as the temperature change ($\Delta T(t)$) of the calorimeter cell; $\Delta H_c(t) = C \Delta T(t)$, where C was the gross heat capacity of the cell.

3. Results

3.1. Characterization of enthalpy relaxations in solid solutions

It is known that a glass transition takes place in the crystalline state of pure dibenzofuran and fluorene at 316 K [11]. Heat capacities of solid solutions were thus measured in the range 250–350 K by an intermittent heating method under adiabatic conditions. Spontaneous

temperature drifts were observed for all the solid solution samples in the temperature-rating periods during the series of measurements. Open circles in figure 2 represent temperature dependences of the drift rates of the samples pre-cooled at about 10 K min^{-1} through the glass transition region. The spontaneous exothermic effect started to be observed at around 260 K, showed its maximum and turned over to the endothermic effect at around 300–310 K. The maximum of the endothermic effect appeared at only a slightly lower temperature as the second component was doped in and the drift returned to normal at around 320–330 K. Figure 3 shows temperature-dependences of heat capacities of the solid solutions. A heat capacity jump was found in the range 310–320 K for all the samples in association with the systematic appearance of the spontaneous exothermic/endothermic drifts. These phenomena are characteristic of a glass transition [1, 4].
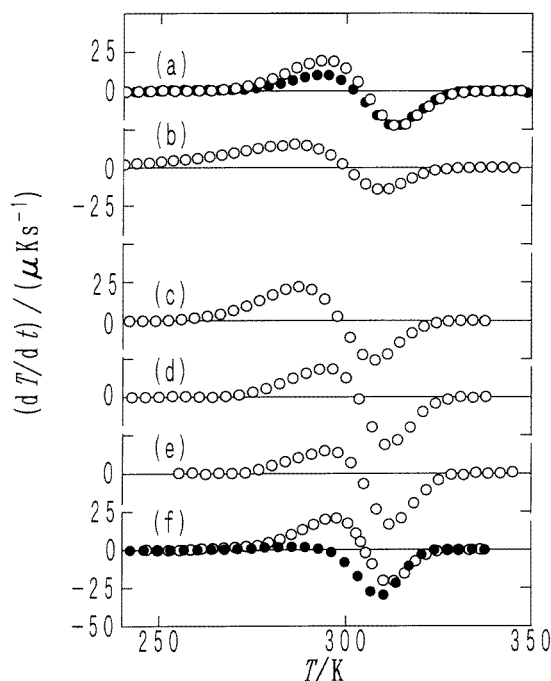

Figure 2. Spontaneous temperature drift rates observed during the series of heat capacity measurements in the crystalline state of solid solution systems between dibenzofuran and fluorene, $(C_{12}H_8O)_{1-x}(C_{13}H_{10})_x$: (a), $x = 1$; (b), $x = 0.8501$; (c), $x = 0.1001$; (d), $x = 0.0243$; (e), $x = 0.0066$; and (f), $x = 0$. Open circles represent the results of the samples pre-cooled at the rate of about 10 K min^{-1} before the measurements and full circles represent those of the samples pre-cooled at rates smaller than 10 K min^{-1}.

Figures 4–7 show data of temperature drifts tracked for a long time at around 300 K after each temperature jump in $(C_{12}H_8O)_{1-x}(C_{13}H_{10})_x$ ($x = 0$, 0.0243, 0.1001 and 1, respectively); the samples were kept for a long enough time (about 3 days) to attain the equilibrium states at the respective desired temperatures before the sudden temperature jumps. The enthalpy which should relax ($\Delta H_c(0) = C\Delta T(0)$, where C is the gross heat capacity of the calorimeter cell, about 40 J K^{-1} at 300 K) was in proportion to the magnitude of the temperature jump. The relaxation processes showed non-exponential properties and
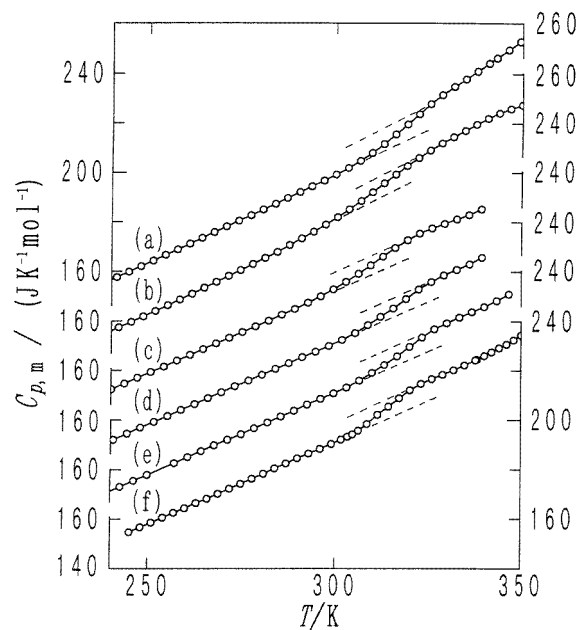
Figure 3. Molar heat capacities of solid solutions $(C_{12}H_8O)_{1-x}(C_{13}H_{10})_x$ in the glass transition region: (a), $x = 1$; (b), $x = 0.8501$; (c), $x = 0.1001$; (d), $x = 0.0243$; (e), $x = 0.0066$; and (f), $x = 0$. The upper and lower broken lines indicate the assumed heat capacity curves in the equilibrium and the frozen-in states, respectively, with respect to the reorientational degree of freedom of the molecule relevant to the glass transition.
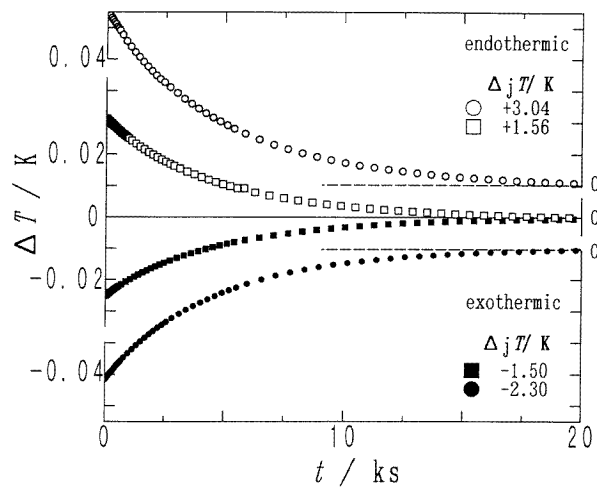

Figure 4. Enthalpy relaxation processes at 304 K in dibenzofuran after each sudden temperature jump.

were analysed by using the stretched exponential function [16]

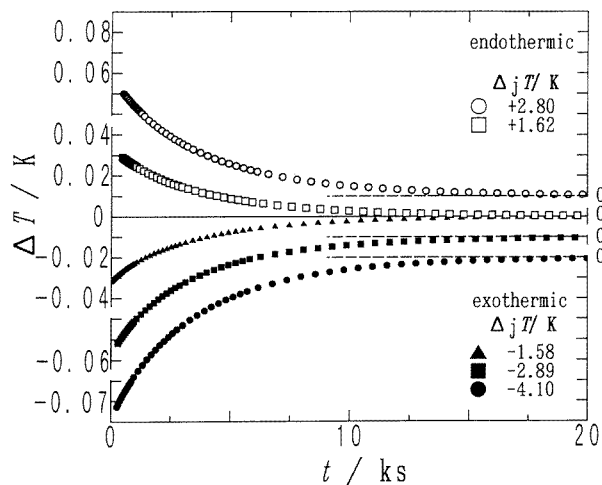$$\Delta T(t) = \Delta T(0) \exp[-(t/\tau)^{\beta}] \qquad 0 < \beta \leqslant 1 \tag{1}$$

Figure 5. Enthalpy relaxation processes at 304 K in a solid solution of constitution $(C_{12}H_8O)_{0.9757}(C_{13}H_{10})_{0.0243}$ after each sudden temperature jump.
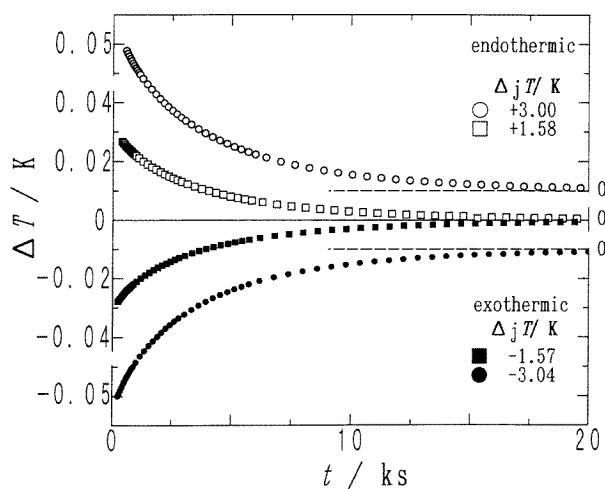

Figure 6. Enthalpy relaxation processes at 300 K in a solid solution of constitution $(C_{12}H_8O)_{0.8999}(C_{13}H_{10})_{0.1001}$ after each sudden temperature jump.

where τ and β denote a characteristic time and a non-exponentiality parameter, respectively. This equation is transformed to the following form by taking its double logarithm:

$$\log\{\log[\Delta T(0)/\Delta T(t)]\} = \beta \log(t/\tau) - 0.3623. \tag{2}$$

The non-exponential parameter β is then given by the slope of the plots of the left-hand side of equations (2) versus $\log t$. Figure 8 shows the plots of the data in figures 4–7 and the linear relation indicates a good fitting of the data by the stretched exponential function. The β values were determined from the slopes and are plotted as a function of the temperature jump in figures 9 and 10 for the solid solution systems of dibenzofuran doped with a small amount of fluorene and conversely of fluorene doped with a small amount of
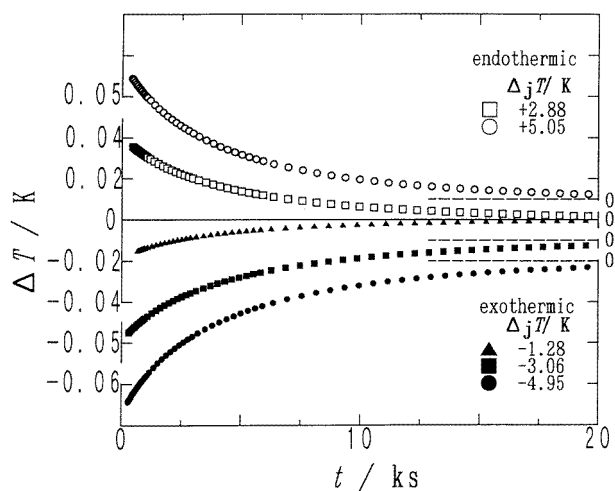
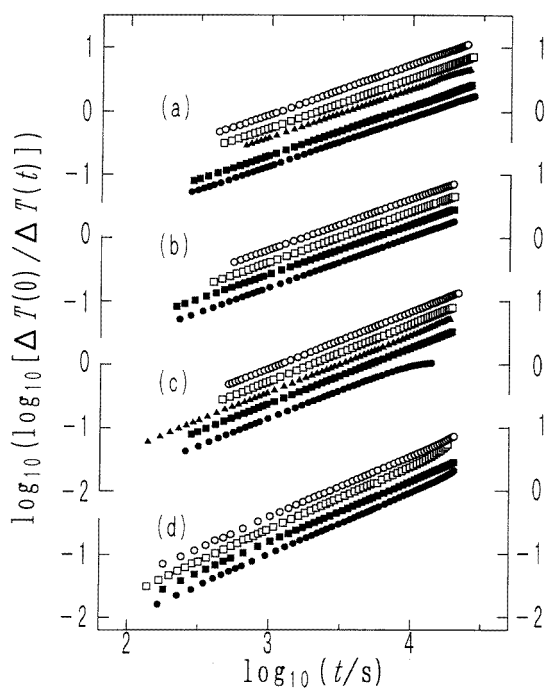**Figure 7.** Enthalpy relaxation processes at 300 K in fluorene after each sudden temperature jump.

Figure 8. Fitting of the endothermic and exothermic enthalpy relaxation processes in solid solutions $(C_{12}H_8O)_{1-x}(C_{13}H_{10})_x$: (a), $x = 1$; (b), $x = 0.1001$; (c), $x = 0.0243$; and (d), $x = 0$. The marks correspond to those in figures 4–7. Since all the sets of data for each composition fall almost on the same straight line, the plots are shifted upwards by 0.2 in order of increasing $\Delta_j T$; the ordinate scale corresponds to the data represented by full circles.

dibenzofuran, respectively. From figures 9 and 10, two facts should be pointed out. First, the β values are essentially independent of the sign and magnitude of the temperature jump
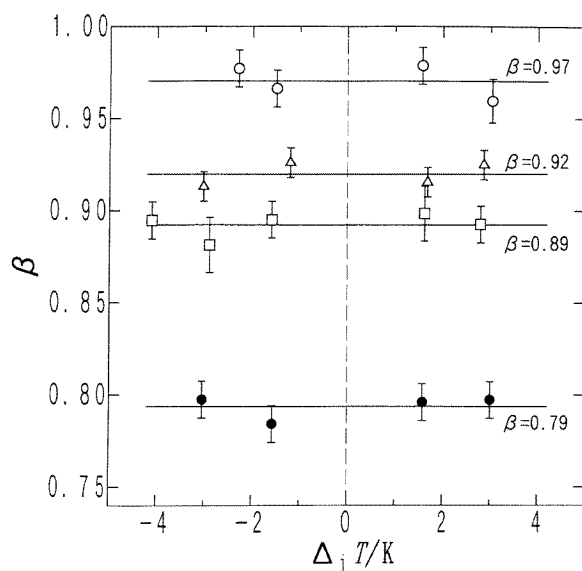
Figure 9. The dependence of the non-exponentiality parameter β on the magnitude of the temperature jump in pure dibenzofuran and its solid solutions doped with fluorene, $(C_{12}H_8O)_{1-x}(C_{13}H_{10})_x$: ($\bigcirc$), $x = 0$; ($\triangle$), $x = 0.0066$; ($\square$), $x = 0.0243$; and ($\bullet$), $x = 0.1001$.
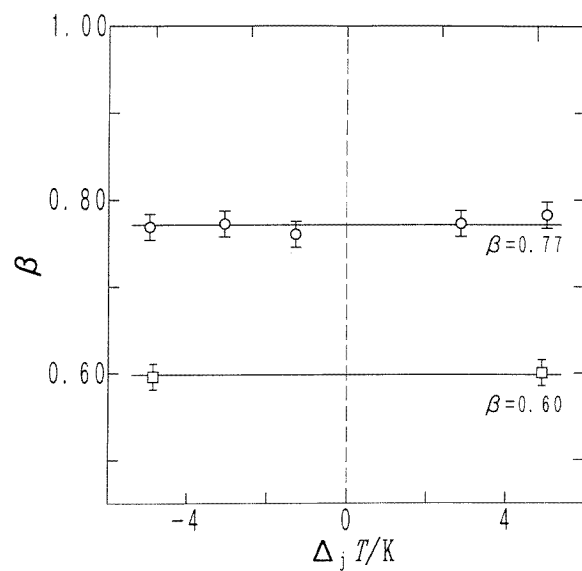

Figure 10. The dependence of the non-exponentiality parameter β on the magnitude of the temperature jump in pure fluorene and its solid solution doped with dibenzofuran, $(C_{12}H_8O)_{1-x}(C_{13}H_{10})_x$: ($\bigcirc$), $x = 1$; and ($\square$), $x = 0.8501$.

for each compound. This means that the relaxation functions show linearity with respect to the magnitude of the temperature jump. This linearity in the solid solution systems
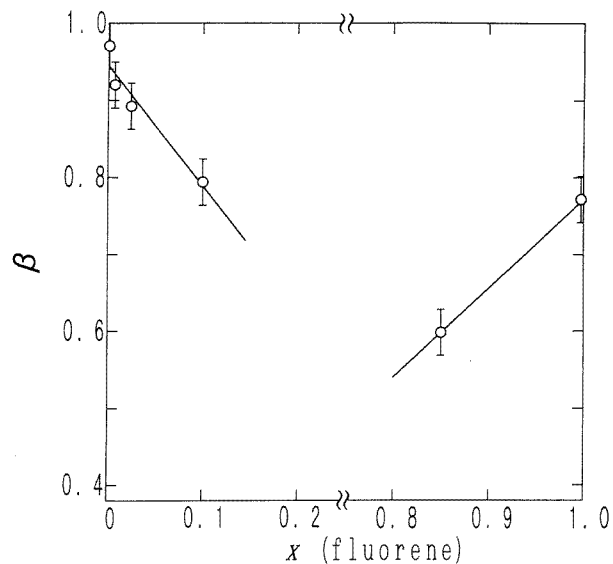
Figure 11. The composition-dependence of the non-exponentiality parameter (β) in solid solution systems between dibenzofuran and fluorene.
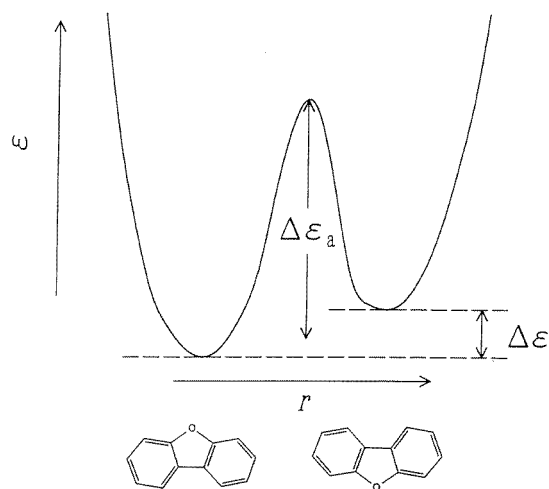

Figure 12. A double-well potential curve representing any microscopic configurational change: ε is the potential energy, $\Delta\varepsilon_a$ is the potential barrier, $\Delta\varepsilon$ is the energy difference between two potential minima and r is the configurational coordinate. Two structural formulae of dibenzofuran drawn in the bottom portion represent the two accessible orientations in the crystalline state and the two orientations are assigned to the two states of potential minima on the curve.

is quite in contrast to the result in liquids. Second, the β value decreases upon adding the second component into a pure substance. Figure 11 shows the β values against the composition x. In view of the fact that the addition of a second component into a pure
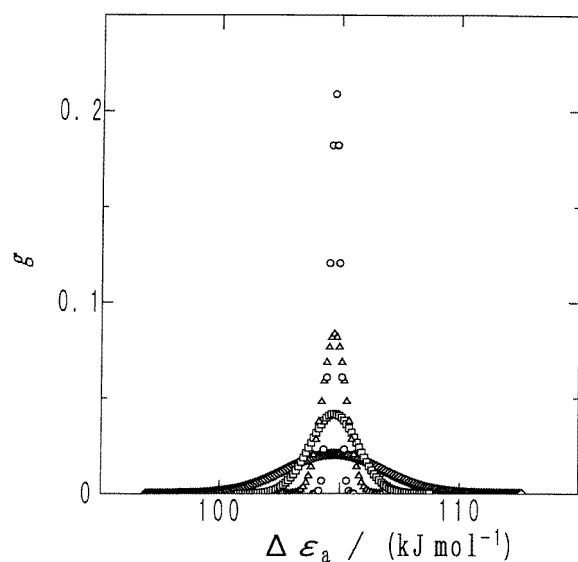
Figure 13. Gaussian distributions of activation energies. The probability density (g) corresponds to the weighting factor in equation (5). σ denotes the root mean square deviation of the activation energies: ($\bigcirc$), 0.2; ($\triangle$), 0.5; ($\square$), 1.0; and ($\diamond$), 2.0 J K mol^{-1}.
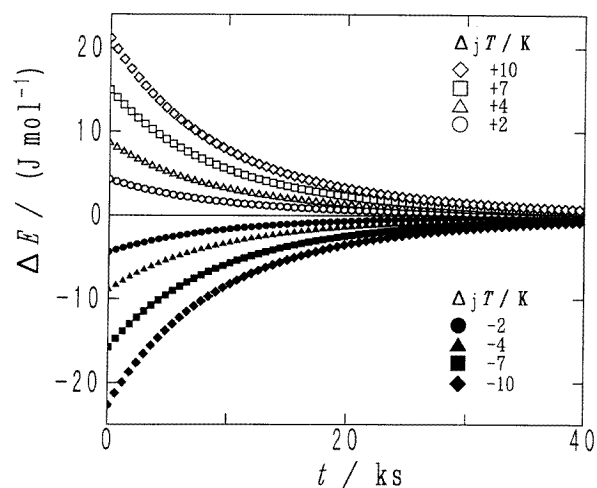

Figure 14. Computer simulation results of energy relaxation processes in the systems with a Gaussian distribution of activation energies. $\Delta\varepsilon_a$, $\Delta\varepsilon$ and σ were taken to be 104.76, 1.05 and 1.0 kJ mol^{-1}, respectively.

substance introduces some distribution of activation energies and thus relaxation times into the system, the presence of the distribution is concluded to bring about a decrease in the β value, namely to enhance the degree of non-exponentiality of the relaxation function as a whole.
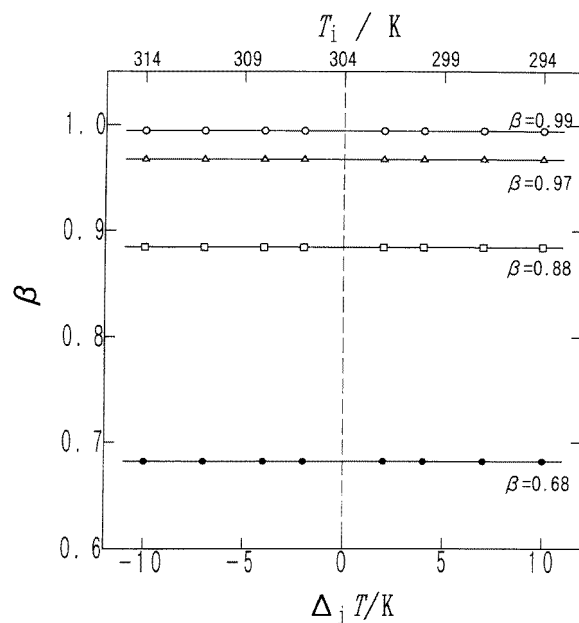
Figure 15. The temperature-jump-dependence of the non-exponentiality parameter (β) of a stretched exponential function fitted to the simulated relaxation processes: (O), 0.2; ($\triangle$), 0.5; ($\square$), 1.0; and ($\bullet$), 2.0 J K mol^{-1} for the root mean square deviation (σ) of activation energies.

3.2. Computer simulation of the structural relaxation system with a distribution but without temperature change in the activation energies

Solid solution systems with only a small fraction of disorder remaining showed non-exponential and linear behaviours in the enthalpy relaxations as described above. The non-exponential behaviour was concluded to have been due to the presence of a distribution in activation energies, whereupon the linear property, in contrast to the nonlinear one in glassy liquids, would be due to the essential constancy of activation energy for the reorientation of each molecule, namely to the Arrhénius behaviour of relaxation times.

Figure 12 shows a double-well potential curve which represents the energetic situation for any microscopic configurational change and, as an example, the reorientation of dibenzofuran is illustrated in the bottom portion. $\Delta\varepsilon$ is the energy difference between two energy minima and determines the static properties such as the heat capacity contribution with respect to the configurational degree of freedom. The states of the minima correspond to two accessible orientations of the molecule in the present systems. The probabilities of a molecule being in the energetically correct and wrong orientations (p_1 and p_2 respectively) are given by the following Boltzmann distribution:

$$p_1 = \frac{1}{1 + \exp[-\Delta\varepsilon/(RT)]} \qquad p_2 = \frac{\exp[-\Delta\varepsilon/(RT)]}{1 + \exp[-\Delta\varepsilon/(RT)]} \tag{3}$$

respectively. p_1 and p_2, as a matter of course, change both with temperature and with $\Delta\varepsilon$. $\Delta\varepsilon_a$ is the activation energy for the configurational change and determines the relaxation times essentially according to the Arrhénius equation

$$\tau = \tau_0 \exp[\Delta\varepsilon_a/(RT)] \tag{4}$$

where τ_0 is a pre-exponential factor taken to be 10^{-14} s in the present simulation [7]. The distribution of the activation energies was tentatively expressed by the following Gaussian distribution:

$$g(\Delta\varepsilon_a) = (2\pi\sigma^2)^{-1/2} \exp\{-[\Delta(\Delta\varepsilon_a)]^2/2\sigma^2\} \tag{5}$$

where σ^2 is the mean square deviation of activation energies ($\overline{[\Delta(\Delta\varepsilon_a)]^2}$).

Figure 13 shows distributions of activation energies in cases with $\sigma = 0.2, 0.5, 1.0$ and 2.0 kJ mol^{-1}, respectively. Here the average activation energy ($\overline{\Delta\varepsilon_a}$) was fixed at 104.76 kJ mol^{-1} in order to give the glass transition temperature of 300 K, which was close to those in the present systems. $\Delta\varepsilon$ was taken to be constant at 10.476 kJ mol^{-1}, 10% of $\overline{\Delta\varepsilon_a}$, and the relaxation processes were calculated by summing up the contributions from each processes with different $\Delta\varepsilon_a$ values:

$$\phi(t) = \sum_k \omega_k \exp(-t/\tau_k). \tag{6}$$

By way of an example of the simulation, relaxation processes with a distribution of $\sigma = 1$ kJ mol^{-1} are shown in figure 14. The relaxation processes were tracked at the temperature at which the average relaxation time became 10^4 s. The plots are given for the relaxations after sudden temperature jumps of $+10, +7, +4, +2, -2, -4, -7$ and -10 K in order from the top to the bottom curves, respectively. All the relaxation processes fitted in terms of the stretched exponential function gave exactly same non-exponentiality parameter (β) and time constant (τ), respectively. The obtained values of β are plotted in figure 15 as a function of $\Delta_j T$ and show the following two characteristics. First, the β values are definitely independent of $\Delta_j T$ for each fixed σ, indicating that the relaxation function is linear with respect to the $\Delta_j T$. This means that the linearity of the relaxation function follows from the Arrhénius property of relaxation times. Second, the β values decrease remarkably with increasing σ, indicating that β reflects the distribution of activation energies. These results are in complete agreement with the above experimental enthalpy relaxation results in solid solution systems of glassy crystals. Therefore, the decrease in β with doping of the second component into pure dibenzofuran or fluorene is reasonably concluded to originate from the broadening in the distribution of activation energies for the reorientation of molecules. This is quite probable in that different molecules give rise more or less to different molecular interactions and find different potential curves for their reorientations.

4. Discussion and conclusion

The properties of irreversible relaxation processes in solid solution systems were investigated with dibenzofuran and fluorene having only a small fraction of orientational disorder. They were computer-simulated and characterized by the presence of a distribution in the relaxation times and by the Arrhénius behaviour of the relaxation time for each elementary process.

The linear property of the relaxation functions with respect to the temperature jump was found both in the experiment and in the computer simulation. This property is quite in contrast to the result for glassy liquids [12, 13] and is suggestive of the origins of complex relaxation properties in liquids. The essential point of difference between the stable glassy crystal and glassy liquid concerning the irreversible structural relaxations is that the arrangement of molecules does not change essentially in the former, resulting in no change in the activation energies for each reorientation with the progress of relaxation whereas it does in the latter, resulting in the change in the activation energies. The change in the arrangement of molecules in the liquid is related to the clustered structure and its

change with temperature, and thus to the non-Arrhénius property of relaxation times. In fact, we found a good linear relation between the nonlinearity of the relaxation function and the non-Arrhénius property, namely the fragility of the liquid [8, 9]. Thus the present result verifies that the nonlinearity of irreversible relaxation functions in liquids is closely related to the non-Arrhénius property of relaxation times, but is primarily irrelevant to the presence of distribution in the relaxation times, namely to the value of the non-exponentiality parameter (β_0) at $\Delta_j T = 0$ K.

Acknowledgment

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