Temperature Dependence of Diffusion in 3-Methylpentane/Methylcyclohexane Mixtures Above Their Glass Transition Temperatures

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Abstract

The temperature dependences of the phosphorescence decay from the triplet state of naphthalene embedded in 3-methylpentane/methylcyclohexane mixtures of different compositions in the presence and absence of oxygen have been determined and are presented as Arrhenius plots. In the presence of oxygen, the slopes of these plots above the glass transition temperature depend on the composition of the mixture. It is shown that the effect of solvent composition in this temperature region can be explained by interactions between the solvent molecules which affect the activation energy of diffusion of the oxygen which is quenching the triplet state of naphthalene.

In the absence of oxygen, the effect of solvent mixture composition is small, and it is suggested that the deactivation of the triplet state is affected by steric constraints imposed by the surrounding molecules.

Introduction

Low-temperature organic glasses have been widely used as trapping matrices in the study of free radicals. Ling and Willard[1,2] have examined the viscosities of a number of these glasses below their glass transition temperatures in an effort to gain a better understanding of the decay of trapped species. However, at these temperatures translational molecular movement is very limited. We were therefore interested in extending some of their studies into the region above the glass transition temperature, T_g, where bimolecular decay processes involving diffusion of molecules or molecular fragments are expected to become important.

In particular, Ling and Willard have studied the temperature dependence of viscosity for a number of 3-methylpentane/methylcyclohexane mixed glasses below T_g. In this paper we report the results of our work on the temperature dependence of diffusion in these mixtures above T_g.

Experimental

Method

The rate of reaction of a triplet state species with oxygen can be determined from the decay of phosphorescence. For a given triplet state species the rate of reaction is proportional to the diffusion coefficient of the solvent[3,4] and therefore the temperature dependence of diffusion can be determined from the temperature dependence of the phosphorescence decay in the presence of oxygen.

[1] Ling, C. A., and Willard, J. E., *J. Phys. Chem.*, 1968, **72**, 3349.
[2] Ling, C. A., and Willard, J. E., *J. Phys. Chem.*, 1968, **72**, 1918.
[3] Chandrasekhar, S., *Rev. Mod. Phys.*, 1943, **15**, 1.
[4] Benson, R., and Geacintov, N. E., *J. Chem. Phys.*, 1973, **59**, 4428.

Light from a medium-pressure mercury arc (Philips 57201E) was focused into a quartz cell containing a 10^{-3} M solution of naphthalene in the hydrocarbon mixture. The cell was surrounded by a copper block and the lower end of this block was immersed in liquid nitrogen. A heater wire wound around the block made it possible to adjust and control the temperature of the cell and its contents. Emission from the naphthalene solution was detected at right angles to the exciting beam by a 1P28 photomultiplier tube. A camera shutter was placed in the exciting beam and after closing this shutter the decay of phosphorescence was recorded. Decays at a number of temperatures from 80 K up to about 120 K were recorded from oxygen-saturated solutions of different 3-methylpentane/methylcyclohexane composition. Similar experiments were done on solutions from which oxygen had been removed by a number of freeze–pump–thaw cycles. The rate constants, k, of the decays were determined and the $\ln k$ values obtained at different temperatures, T, for a given solution were plotted against T^{-1}. Above T_g all decay rate constants increase rapidly with increasing temperature and may be described by the equation:

$$\ln k = A_k + B_{k(>)} T^{-1} \tag{1}$$

(The subscript $(>)$ signifies that the parameter is associated with data above the glass transition temperature.) The parameter $B_{k(>)}$ was obtained for each solution by a least-squares fit of the data, above T_g, to equation (1). (The glass transition temperature, T_g, was taken to be the temperature above which $\ln k$ begins to increase rapidly.)

Materials

The naphthalene used was purified by a multipass zone-refining process. The solvents, 3-methylpentane and methylcyclohexane, were Phillips 'Pure Grade' ($>99\%$). They were both purified by stirring with fuming sulphuric acid for 50 h, washing with distilled water and drying over anhydrous calcium chloride. They were then vacuum-distilled and stored over a sodium mirror.

The compositions of the solvent mixtures were determined following the phosphorescence decay measurements by gas chromatography on an SE-30 column. It was not possible to work with mixtures above a methylcyclohexane mole fraction of about $0 \cdot 75$ because the glasses formed on cooling these mixtures cracked badly and broke the quartz cell.
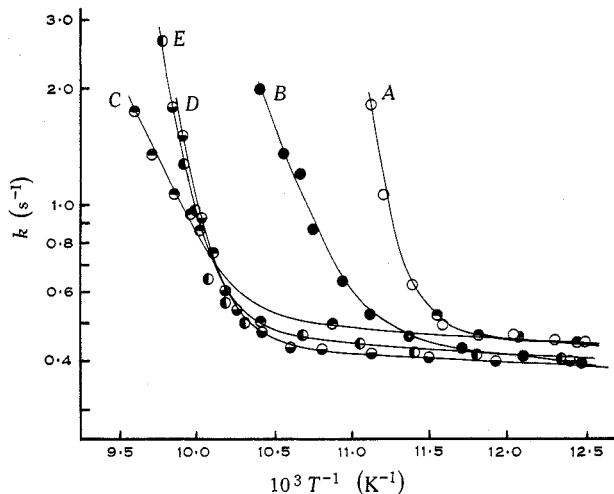

Fig. 1. Plots of $\ln k$ against T^{-1} for different compositions of oxygen-saturated solutions of 3-methylpentane/methylcyclohexane. Mole fractions of methylcyclohexane: A, $0 \cdot 00$; B, $0 \cdot 34$; C, $0 \cdot 55$; D, $0 \cdot 68$; E, $0 \cdot 82$.

Results

A series of plots of $\ln k$ against T^{-1} for the oxygen-saturated solutions of different composition is shown in Fig. 1. The parameter, $B_{k(>)}$, for these curves in the region above T_g depends on the solvent composition. This is displayed in Fig. 2 (curve A).

At temperatures below the glass temperature Ling and Willard[1] have shown that the temperature dependence of viscosities, η, of 3-methylpentane/methylcyclohexane can be expressed as

$$\ln \eta = A_\eta + B_{\eta(<)} T^{-1}$$

(The subscript $(<)$ signifies that the parameter is associated with data below the glass temperature.) The dependence of the slope, $B_{\eta(<)}$, of the line resulting from plotting $\ln \eta$ against T^{-1} on composition of the mixture is shown in Fig. 2 (curve B).

Fig. 2. Dependence of parameter B_k or B_η on composition of mixture. A, $B_{k(>)}$ for oxygen-containing solutions above the glass temperature; B, $B_{\eta(<)}$ for solutions below the glass temperature. Data derived from Ling and Willard's results.[1] C, $B_{k(>)}$ for degassed solutions above the glass temperature.
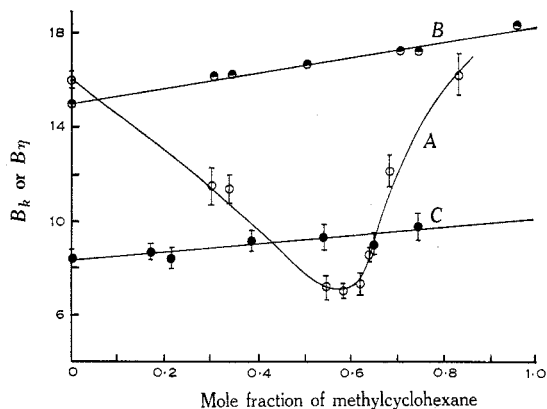
The dependence of $B_{k(>)}$ on mixture composition in solutions where no oxygen is present is shown in Fig. 2 (curve C).

Discussion

(a) In the Presence of Oxygen

Assuming that the viscosity is inversely proportional to the diffusion coefficient, the magnitudes of $B_{k(>)}$ and $B_{\eta(<)}$ may be compared directly. The difference in the behaviour of these two quantities with change in mixture composition (see Fig. 2) reflects a difference between the transport process operating at $T > T_g$ and at $T < T_g$. It is possible to explain this difference in terms of the theories of diffusion and viscosity applicable to binary mixtures. These take account of interactions between the different component molecules with an excess free energy of mixing term and include another term to express the requirement for a vacancy of sufficient size being present to allow a molecule to move from one site to another.

Following Bloomfield and Dewan,[5] the viscosity, η, of a binary mixture can be expressed as

$$\ln \eta = X_1 \Delta G_1/RT + X_2 \Delta G_2/RT - \Delta G^R/RT + V^*(1/V_f - X_1/V_{f1} - X_2/V_{f2}) \qquad (2)$$

where X is the mole fraction, ΔG is the free energy of mixing, subscripts 1 and 2 refer to components 1 and 2 respectively, ΔG^R is the residual free energy of mixing, V^* is the minimum empty volume which must be available for jumping between sites, V_f is the 'free volume' which is temperature dependent and $(V_f - V^*)$ is associated with the average molecular cage volume. (A similar expression could be written

[5] Bloomfield, V. A., and Dewan, R. K., *J. Phys. Chem.*, 1971, **75**, 3113.

for the diffusion coefficient.) Following Macedo and Litovitz,[6] if the thermal expansion coefficient, α, is constant over the temperature range of interest and if temperatures in this range are much greater than the apparent temperatures at which the 'free volume' becomes zero, then $V_f = \alpha V T$ and equation (2) becomes

$$\ln \eta = A + (\Delta G_1 + \Delta G_2 - \Delta G^R + 1/\alpha V - X_1/\alpha_1 V_1 - X_2/\alpha_2 V_2)/RT$$

From this it is apparent that $[\mathrm{d}\ln\eta/\mathrm{d}(T^{-1})]$ i.e. B_η (and the same holds for B_k) contains a non-linear composition term associated with the free energy of mixing and with a 'free-volume' term. It has been found that each of these terms can dominate the temperature dependence of transport in different temperature regions. For example, transport in B_2O_3 glass is dominated by the free energy of mixing term at high temperatures and by the 'free volume' at lower temperatures.[6] In most supercooled liquids the transport processes tend to be governed by the 'free volume'.[6]

In view of this discussion, in 3-methylpentane/methylcyclohexane mixtures, below T_g (Ling and Willard's results) the transport process is 'free volume' limited while above this temperature (our results) the non-linear term associated with free energy of mixing assumed importance.

(b) In the Absence of Oxygen

The temperature dependence of phosphorescence decay increases slowly and monotonically with methylcyclohexane mole fraction, in contrast to the behaviour exhibited by solutions containing oxygen. This suggests that transport phenomena such as quenching by a trace impurity[7,8] cannot account for the results. However, the solvent must play an important part in determining the rate of triplet state deactivation. This is shown by the rapid increase in rate of phosphorescence decay at the temperatures above the glass transition temperature. A similar effect is described by Melhuish[9] for the radiationless decay of benzophenone in poly(methyl methacrylate) above the temperature associated with a second-order phase transition in the polymer. He suggested that the rapid increase in rate of deactivation resulted from the release of some steric constraint on the triplet state molecule as the medium relaxes. The temperature dependence of viscosity of these mixtures displayed in Fig. 2 suggests that the molecular 'free volume' available increases monotonically with increasing mole fraction. The observation that $B_{k(>)}$ for deoxygenated solutions behaves in a similar fashion is consistent with the idea that the medium exerts some spatial constraint on the triplet state molecule which, when relaxed, favours deactivation of the excited state. Results of experiments by Jones and Calloway[10] are interpreted in the same way.

Conclusions

Transport in 3-methylpentane/methylcyclohexane mixtures appears to be determined by 'free-volume' considerations at temperatures below their glass transition

[6] Macedo, P. B., and Litovitz, T. A., *J. Chem. Phys.*, 1965, **42**, 245.

[7] Jones, T. H., and Livingston, R., *Trans. Faraday Soc.*, 1964, **60**, 2168.

[8] Livingston, R., and Ware, W. R., *J. Chem. Phys.*, 1963, **39**, 2593.

[9] Melhuish, W. H., *Trans. Faraday Soc.*, 1966, **62**, 3384.

[10] Jones, P. F., and Calloway, A. R., *J. Chem. Phys.*, 1969, **51**, 1661.

temperature. Above this temperature interactions between the two different solvent molecules (which can be expressed in the excess free energy of mixing resulting in an activation energy of diffusion) become important.

In the absence of oxygen, the rate of deactivation of the triplet state species appears to be affected by steric constraints imposed by the surrounding solvent molecules.