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The nature of the β process for polar solutes in four glassy forming solids

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Dielectric constant and loss data have been obtained for several rigid dipolar substituted benzenes in up to four glass forming solvents. Measurements were made between 10 and 10^5 Hz from about 80 K up to room temperature. The broad loss curves were analyzed to give relaxation times which were then used to determine Eyring activation enthalpies ΔH_E. For the glassy systems dipole reorientation, at temperatures well below the glass transition, T_g is essentially independent of the solvent and is identified as a β process. The ΔH_E values of the β process increase appropriately with molecular size but are largely independent of the glassy medium. The β process for these systems is ascribed to molecular relaxation which may possibly occur in a "solvent cavity."

INTRODUCTION

The rotation of simple dipolar organic molecules as pure liquids or in nonpolar solvents at room temperature gives rise to dielectric dispersion at microwave frequencies.[1] Dipole reorientation may be slowed down to such an extent that the absorption occurs in the kHz region by the employment of a glass forming solvent.[2] At temperatures just above the glass transition the relaxation involves a highly cooperative characterized by a large apparent activation enthalpy ΔH_E. When the system is cooled into the glassy state, a relaxation process often persists.[3] These secondary relaxations, which have a much smaller ΔH_E, are observed for rigid molecules which cannot undergo reorientation by any intramolecular process.

α and β processes have been observed for various systems which form glasses and these include: (a) pure o-terphenyl[2,4]; (b) cis-decalin[2,4]—only an α process has been detected; (c) solutes in cis-decalin[2,6,7]; (d) various other supercooled liquids[2,4,5]; (e) mixtures of polar liquids[2,4,8]; and (f) amorphous polymers.[7]

A variety of studies has been made on the glassy forming substances cis-decalin and o-terphenyl. In both cases solutes have been added (usually at high concentration) and α and β processes have been detected above and below the T_g in both cases. The exact nature of the β process in these systems has never been precisely identified. The analogy which is made to the behavior of solid polymers is appealing—especially with respect to the α process. However, for the β process, the relaxation may be somewhat vague—especially since the precise nature of the β process in most polymers has never been established.

Various interpretations of the β processes in glasses of rigid molecules have been made, and most of these have been considered by Johari and Goldstein,[4] Johari,[15] and Williams.[2]

The present work examines two simple polar solutes at low concentrations in cis-decalin and o-terphenyl. The work has been extended by the examination of a variety of polar solutes in a polystyrene matrix and in o-terphenyl and Santovac as well. Thus, in two cases, all four media have been used.

It was considered worthwhile to attempt to relate the results obtained in the solvent media, cis-decalin, o-terphenyl, and Santovac, with those in polystyrene, where it had been well established that for a rigid molecule at low concentration, the relaxation process is a molecular one.[9,10] This was first established by Davies and Swain.[9] A suitable parameter to carry out this comparison of the low temperature (β) process in all four media is the enthalpy of activation.

EXPERIMENTAL

Dielectric constant ϵ' and loss ϵ'' values were obtained between 10 and 10^5 Hz by means of a general radio 1616 precision capacitance measurement system. A three-terminal circular parallel plate capacitance cell was employed for the polystyrene matrix samples. The other samples were measured in a three-terminal coaxial cell. In all cases, the cell was placed in an airtight insulated aluminum chamber and cooled by contact with an insulated liquid nitrogen container. The cell was warmed by the use of heating wire elements, and temperature control to ± 0.1 K was achieved with a thermoregulator.

All of the chemicals were available commercially and were dried prior to use. The solvent, Santovac, is a six-ring, meta-linked, polyphenyl ether, bis-m(m-phenoxy phenoxy) phenyl ether, which is available from Monsanto Ltd. The preparation of samples dispersed in a polystyrene disk has been described previously.[11] The other solutions were heated to about 335 K to facilitate solution or in the case of o-terphenyl to melt the solvent. In order to ensure a homogeneous solution, the samples were allowed to stand for about 24 h. They were then reheated to about 335 K and placed in the dielectric cell which had also been heated to this temperature. For all of the samples the cell was quickly cooled to ~ 77 K and then heated to the temperature region of dispersion. The results were reproducible when the procedure was repeated on the same sample. The solute concentrations were in the region of 8% by weight in the decalin, polystyrene, o-terphenyl, and Santovac solutions.

RESULTS

Some typical dielectric absorption curves are shown in Figs. 1–4. The broad loss curves were analyzed as before[11]

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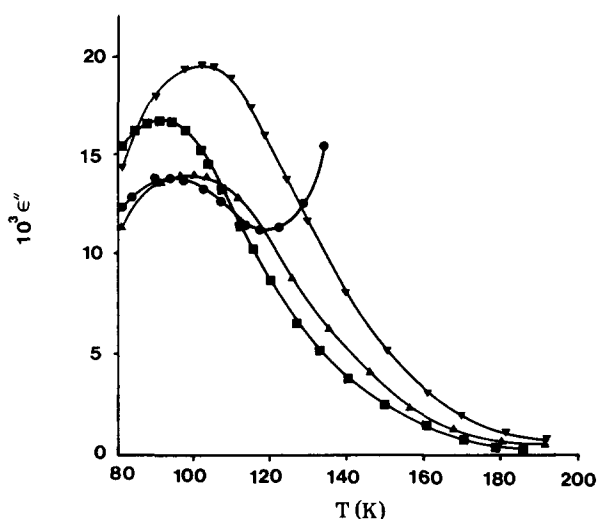
FIG. 1. Dielectric loss ϵ'' at 1 kHz, against temperature T for o-dichlorobenzene in o-terphenyl ▼; polystyrene ■; Santovac ▼; and cis-decalin ●.

using a Fuoss–Kirkwood distribution function to give relaxation times τ and distribution parameters β. Plots of log τT against $1/T$ were used to obtain Eyring activation enthalpies ΔH_E, which are listed in Table I. A sample plot is also given in Fig. 5.

DISCUSSION

Dipolar solutes dispersed in decalin, o-terphenyl, and Santovac show a primary dielectric dispersion just above their glass transition temperature.[4,7,12] This α process involves large scale rearrangements in a viscous medium and is regarded as highly cooperative in nature. It is characterized by broad asymmetric loss curves and a large apparent activa-
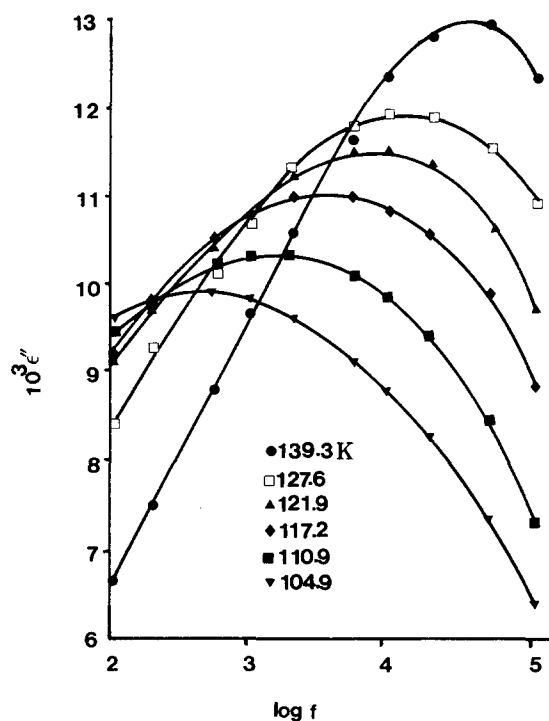

FIG. 3. Dielectric loss ϵ'' against log frequency f for chlorobenzene in o-terphenyl at several temperatures (K) below the glass transition.

tion enthalpy. The temperature/frequency location is largely determined by the T_g of the solution. The polar solute tends to act as a probe on the motions of the often weakly polar solvent. Such α processes are well documented, and characteristic H_E values are available. However, with the exception of polystyrene matrices this is not the case for β processes in glassy forming media although a number of
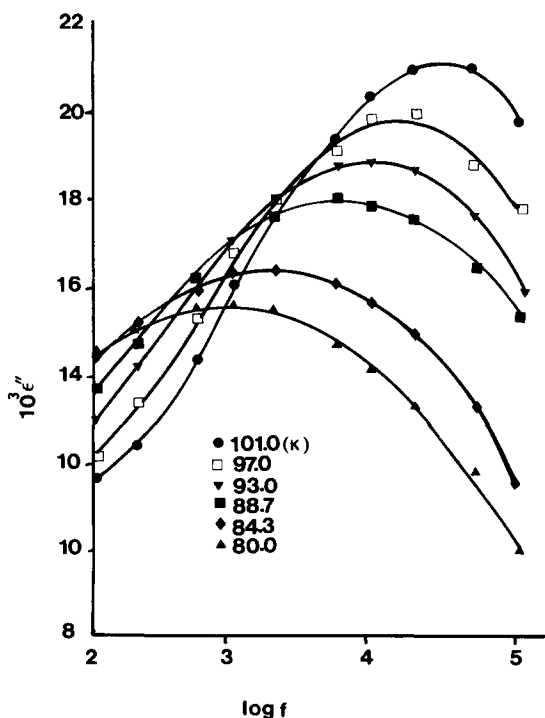

FIG. 2. Dielectric loss ϵ'' against log frequency f for o-dichlorobenzene dispersed in polystyrene at several temperatures (K).
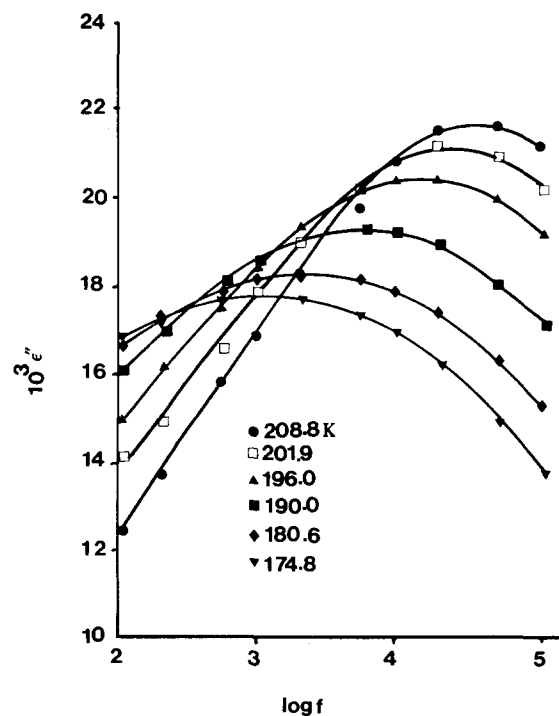

FIG. 4. Dielectric loss ϵ'' against log frequency f for benzonitrile in Santovac at several temperatures (K) below the glass transition.

TABLE I. Activation enthalpy, ΔH_E (kJ mol^{-1}) data for rigid dipolar substituted benzenes in different environments.

Compounds	*cis*-decalin		Polystyrene		*o*-terphenyl		Santovac	
	T	ΔH_E	T	ΔH_E	T	ΔH_E	T	ΔH_E
Fluorobenzene			94–118	9	79– 99	7.0		
Chlorobenzene			80–125	10	99–104	14.4	104–139	16.0
Bromobenzene			101–136	16	115–164	17.4	113–160	18.1
Benzonitrile			133–175	22	166–219	27.4	160–209	28.7
4-chlorotoluene			163–196	26	205–241	28.8	197–240	32.9
o-dichlorobenzene	100–124	12.9	80–103	11.2	80–114	11.4	80–114	13.4
4-methylpyridine	84–106	15.6	88–124	14	105–154	16	110–152	17.2

studies have been made.[4,5,7,12,13] The temperature ranges given in Table I are below the glass transition of the solvent. Polystyrene is a glass at room temperature, and the T_g values of Santovac,[14] *o*-terphenyl,[2] and *cis*-decalin[4] are 270, 243, and 136 K, respectively. Thus, all of the samples given in Table I are in the solid phase. The solvents show only a very small or negligible loss in the temperature regions where the β process occurs.

Two compounds: *o*-dichlorobenzene and 4-methylpyridine have been examined in all four solvents (Table I). For both of these solutes for similar solute concentrations the intensity of the absorption ϵ''_{max} and also the activation enthalpy are similar for each solute in the various solvents (e.g., see Figs. 1 and 5 and Table I). Similarly, for the other solutes listed in Table I both ϵ''_{max} and ΔH_E are relatively independent of the solvent. Such observations have been noted as a characteristic of β relaxation being largely independent of the molecular shape or degree of flexibility or of the type of solvent.[15] As before,[7,10] the ΔH_E values for Santovac are a little larger than those for the other solvents. Johari and Goldstein[5] found a β dispersion for chlorobenzene in *cis*-decalin between 110 and 130 K which is close to the temperatures for the dispersions of this solute in polystyrene, *o*-terphenyl, and Santovac (Table I). These workers did not report a β dispersion for bromobenzene in *cis*-decalin. A variety of reasons have been given for the lack of observation of

a β relaxation in some glasses, and these have been discussed previously.[4,5]

In general, the ΔH_E values for each solute in a particular solvent show an increase with increased molecular size, and the similarity in behavior of the mono-halobenzenes in polystyrene, *o*-terphenyl, and Santovac appears significant. All of the solutes are incapable of exhibiting a dielectrically active, intramolecular motion. The fact that ΔH_E is essentially independent to the solvent implies that there is little interaction between solute and solvent, the latter having little influence upon the rotation of the dipolar solute. For the solute in the polystyrene matrix at these concentrations, the mechanism is well established as molecular relaxation[9,10] where the solute molecules are monomolecularly dispersed in the polystyrene cavities.[1] The virtual identity of the ΔH_E values for *o*-dichlorobenzene in *cis*-decalin, *o*-terphenyl, and Santovac and their correspondence with the polystyrene indicate the molecular nature of the process. This is borne out by similar studies on 4-methylpyridine in all four solvents (Table I). In addition, the ΔH_E values of chlorobenzene, bromobenzene, benzonitrile, and 4-chlorotoluene in polystyrene, *o*-terphenyl, and Santovac lead to identical conclusions.

It is striking that for each of the polar solute molecules in the somewhat diverse glassy materials a similar ΔH_E value results and that the ΔH_E value increases with size appropriate for a molecular process.[10] It is tempting to extend the concept of the single solute molecule (at low concentration) in the polystyrene cavity[1] to the other solvents, the model being that there is a trapped solute molecule (in what is effectively a cavity) where the molecular relaxation takes place between equilibrium positions. On the time scale of the relaxation process the "solvent cavity" does not need to alter appreciably to permit a solute molecule to rotate.

It must be stressed, however, that our findings are for simple rigid molecules in four glassy forming solids. Our concentrations are low compared with most of those employed by the previous investigations on α and β processes such as the studies on mixtures of polar compounds.[4,8] Further, the work on pure supercooled liquids may present a somewhat different case.

A more all-embracing model which leads to a β process in these various systems is one by Johari,[16] where he postulates that a potential exists within the region of the solute molecule which resists rearrangement and leads to relative fixedness of the molecules in that region. Hence, the β-relax-
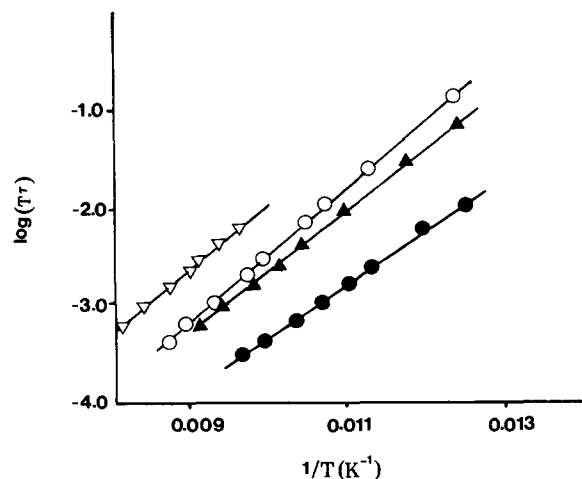

FIG. 5. Eyring rate plot for *o*-dichlorobenzene in Santovac ○; *o*-terphenyl ▼; polystyrene ●; *cis*-decalin ▽.

ation process takes place over this energy barrier. Our systems, which seem to lead to a solvent cavity model for somewhat limited types of systems, would seem in harmony with the more general model conceived by Johari.

Clearly more experimental studies are desirable on other types of simple systems which exhibit such processes, e.g., a wide variety of supercooled liquids of low or even zero dipole moment. This is particularly so since *cis*-decalin exhibits only an α process,[4] whereas *i*-propylbenzene has both an α and a β process.[4] 3-methylpentane gave an α process (with the possibility of a β process at temperatures lower than available)[5] yet its dipole moment is very small and may not be expected to yield either an α or a β process. All three results were obtained by most careful work on highly purified compounds and cannot be readily dismissed as being due to impurity or the presence of moisture.

To conclude, we consider that a wide variety of systems have been studied and reported in the literature many of which bear on the nature of the β process. However, specific detailed study is still required on some of these systems.

ACKNOWLEDGMENTS

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