

Effect of Association Complexes on the Glass Transition in Organic Halide Mixtures

Arnold V. Leslkar

Department of Physics, St. Cloud State University, St. Cloud, Minnesota 56301 (Received September 25, 1975)

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The glass transition temperatures of binary mixtures of chloroform, dichloromethane, and trichloroethylene with several Lewis bases have been measured as a function of composition. The glass transition temperatures of the mixtures are shown to be increased by complex formation between the chloride and the base, and the glass transition temperature is shown to increase with base strength. The chloroform mixtures show the greatest effect of complex formation. A cusp is found in the composition dependence of the glass transition temperature T_g of mixtures of chloroform with triethylamine. The cusp is found at the equimolar composition. It is taken as evidence for the complete association of chloroform with triethylamine into a 1:1 complex at T_g . The trichloroethylene mixtures show greater effects of complex formation than do the dichloromethane mixtures, although evidence from the literature seems to indicate that dichloromethane is the stronger acid.

Introduction

Association between the components of a mixture has been shown to increase the viscosity¹ and thereby the glass transition temperature.² Recent work by Angell and co-workers³ has demonstrated the effect on the glass transition of the formation of a stoichiometric ionic complex in electrolyte solutions. To date, however, no studies of the glass transition illustrating the effect of the formation of stoichiometric molecular complexes in nonelectrolyte solutions have been published. Solutions of the chlorinated hydrocarbons are well suited to such a study. The protons of such hydrocarbons have been shown to be activated to hydrogen bond formation by the attached chlorine atoms.^{4,5} Formation of hydrogen-bonded association complexes between chloroform (CFM) and various organic bases has been demonstrated by calorimetry and various spectroscopic techniques.⁶ Since trichloroethylene (TCE) and dichloromethane (DCM) have also been shown to be capable of serving as electron acceptors in the formation of a hydrogen bond, such complex formation can be expected to occur with these materials as well. In order to examine the effect of this complex formation on the glass transition, the glass transition temperature T_g was measured as a function of composition for binary mixtures of CFM, TCE, and DCM with various electron donors.

Experimental Section

The bases chosen for study were triethylamine (TEA); the ethers, tetrahydrofuran (THF), diethyl ether (DEE), and isopropyl ether (IPE); the carbonyls, acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIK), and benzaldehyde (BZA); the ester, ethyl acetate (EtAC); and the aromatic π donor, toluene. The sources of the materials are listed in Table I. All materials were of reagent grade with the exception of the TEA which was practical grade. All materials were used as received with the exception of acetone and TEA. Because the acetone was common laboratory stock dispensed from a 5-gal drum, it was dried before use by stirring with Drierite, from which it was removed by simple distillation. The TEA was stirred for 2 h or more with KOH pellets from which it was removed by simple distillation. It was then fractionally distilled at a 20

to 1 reflux ratio in a 50 plate Penn State column. The central 80% was taken for measurement. The TEA used in the extrapolations to determine T_g values of the pure organic chlorides was purified by a simpler procedure. Samples of TEA were subjected to simple distillation off of KOH pellets. They were then refluxed with metallic potassium to remove water and again subjected to simple distillation. These samples showed T_g values agreeing to within 1 °C with those of TEA purified by fractional distillation. Because of the tendency of the BZA to oxidize upon exposure to the atmosphere, fresh unopened bottles were frequently exchanged with bottles of the material in use. The water content of all the reagent material was listed by the manufacturer as under 0.2% with the exception of the Baker CFM and the Mallinckrodt BZA for which no water content was given.

Mixtures were prepared gravimetrically. The T_g values were determined by means of differential thermal analysis (DTA) using apparatus previously described.⁷ In the present work the strip chart recorders previously used to record the sample temperature T and the temperature difference ΔT of the sample from the DTA reference material have been replaced by a single X-Y recorder recording ΔT on the vertical axis against T on the horizontal axis. A suitable choice of scale was made to allow recording a 40 deg range of temperature around the glass transition. The T_g values were taken to represent the onset of the transition determined using the procedure of Thompson.⁸ They were found to be reproducible in the present work to within 0.3 °C, and the absolute accuracy is estimated to be 1.5 °C. Absorption of water from the atmosphere during the course of a run was estimated to be less than 0.2% of the sample material by weight by making the tests previously described.⁷

DTA measurements were carried out at a heating rate of 12 deg/min. Samples were contained in 1-mm diameter melting point capillaries. In most of the measurements samples were vitrified by immersion of the sample capillary in liquid nitrogen. It was then inserted into the DTA block, which was maintained under liquid nitrogen. Quenching the sample often leads to a small exothermic peak following the transition.⁹ Because this peak sometimes became confused with the glass transition, making it difficult to deter-

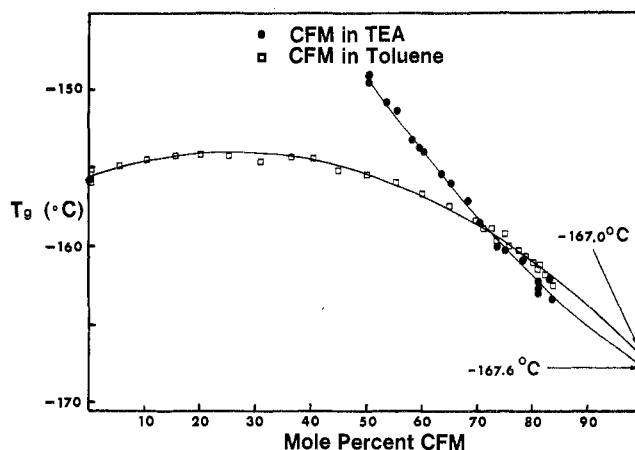
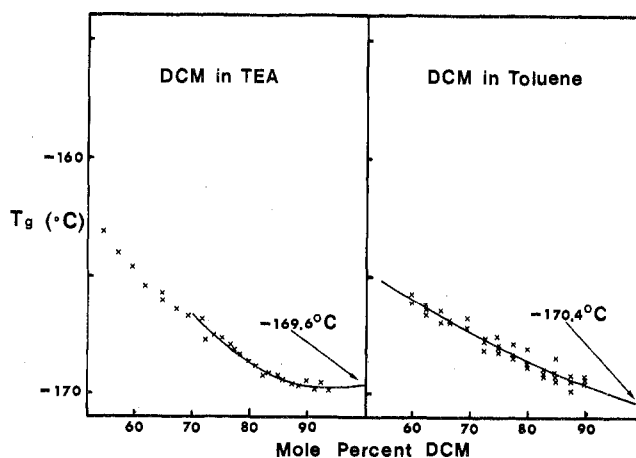
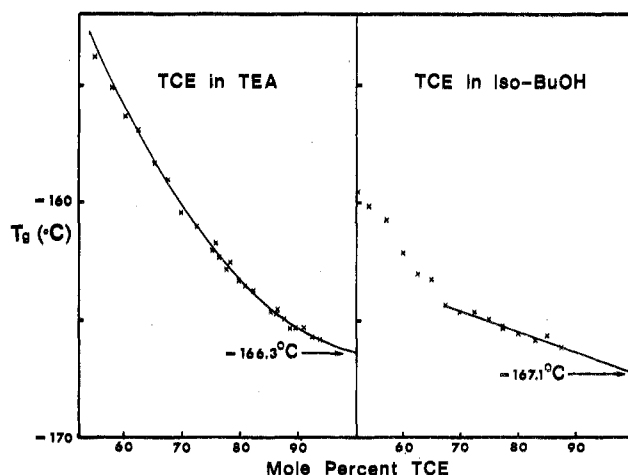
TABLE I: Sources and T_g Values of Solvents

Compound	Manufacturer	T_g , °C
Chloroform (CFM)	Baker, Mallinckrodt	-167.3
Dichloromethane (DCM)	Baker, Mallinckrodt	-170.1
Trichloroethylene (TCE)	Baker, Mallinckrodt	-166.9
Triethylamine (TEA)	Matheson, Eastman	-170.0
Diethyl ether (DEE)	Mallinckrodt	-180.6
Isopropyl ether (IPE)	Mallinckrodt	-171.8
Tetrahydrofuran (THF)	Baker	-193 ± 3
Acetone	Matheson	-173 ± 2.5
Methyl ethyl ketone (MEK)	Mallinckrodt	-161.8
Methyl isobutyl ketone (MIK)	Mallinckrodt	-153.3
Ethyl acetate (EtAC)	Eastman	-155.5
Benzaldehyde (BZA)	Mallinckrodt	-124.1
Toluene	Baker	-155.9

mine T_g , certain samples were rapidly cooled to a point somewhat above T_g but well below their melting point by inserting them into the block at the intermediate temperature. The samples were then slowly cooled through the glass transition by pouring liquid nitrogen directly onto the DTA block. Samples vitrified in this fashion demonstrated a very clean glass transition free of subsidiary peaks. Test measurements on material vitrified by both methods produced T_g values agreeing to better than 1 °C.

Samples were checked for crystallinity by visual inspection. Samples of material to be run by DTA were quenched to liquid nitrogen temperature and then removed from the nitrogen bath. Crystalline areas in the sample were clearly visible as the glass softened. In almost all cases the appearance of crystals under visual inspection was associated with a drastic decrease in the prominence of the glass transition in the DTA record.

The T_g values of the pure solvents are listed in Table I. The uncertainty in each value should be taken to be 1.5 °C unless otherwise indicated. This error represents mainly the overall uncertainty in the temperature measurement. The relative error among the different T_g values is much better than 1 °C. Of the materials listed, toluene, BZA, EtAC, DEE, TEA, and MIK can be vitrified as pure materials, and the values listed for these materials were determined as the means of many direct measurements. THF appears to the eye to vitrify when quenched to the temperature of liquid nitrogen. However, the T_g value is so close to liquid nitrogen temperature that the signature of the transition is lost in the starting transient of the DTA measurement, and the T_g value had to be determined by extrapolation. Similarly, IPE can apparently be vitrified in a capillary tube by quenching in liquid nitrogen. However, the presence of a thermocouple in the sample tube seems to nucleate crystallization so that no direct measurement of the T_g values of this material could be made. The T_g of this material and the remaining solvents were determined by extrapolation. The T_g value for MEK is the mean of extrapolations in six binary mixtures of MEK with CFM, TCE, DCM, reagent methanol, reagent 1-propanol, and reagent 1-butanol. In each mixture the glass transition could be traced to within 90 mol % of the pure MEK. The T_g of IPE is the mean of extrapolations in TCE and DCM mixtures from better than 90 mol % IPE. The THF and acetone T_g values are the result of linear extrapolations in CFM and TCE binary mixtures from 85 mol % or better to

Figure 1. T_g as a function of composition for CFM mixtures: determination of the CFM T_g .Figure 2. T_g as a function of composition for DCM mixtures: determination of the DCM T_g .Figure 3. T_g as a function of composition for TCE mixtures: determination of the TCE T_g .

pure acetone or from 75 mol % or better to pure THF.

The T_g extrapolations for the organic chlorides were made with particular care. The T_g value reported for TCE is the mean of extrapolations in binary mixtures with three different reagent alcohols and with TEA. Examples of these extrapolations are shown in Figure 1. The DCM value

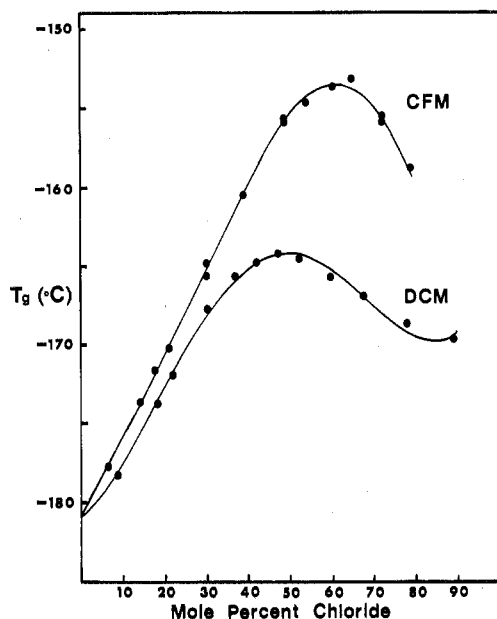


Figure 4. Mixtures of DEE with organic chlorides: T_g as a function of composition.

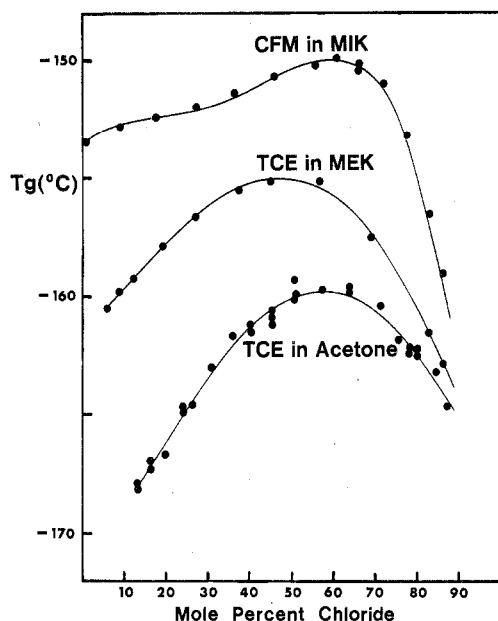


Figure 5. Mixtures of carbonyls with the organic chlorides: T_g as a function of composition.

is the mean of extrapolations in binary mixtures with toluene, TEA, EtAC, and BZA (Figure 2). The CFM value is the mean of extrapolations in binary mixtures with toluene and with TEA (Figure 3).

Results

All possible combinations of chloride proton donors with the bases listed above were studied. Glass formation over wide central ranges of composition was observed even in those mixtures where neither pure component is by itself a glass former. Only in DCM-acetone mixtures and CFM-IPE mixtures was crystallization observed to intervene in the central region of composition. In the former, crystallization was observed over a range of about 20% centered on the equimolar composition, while in the latter mixtures,

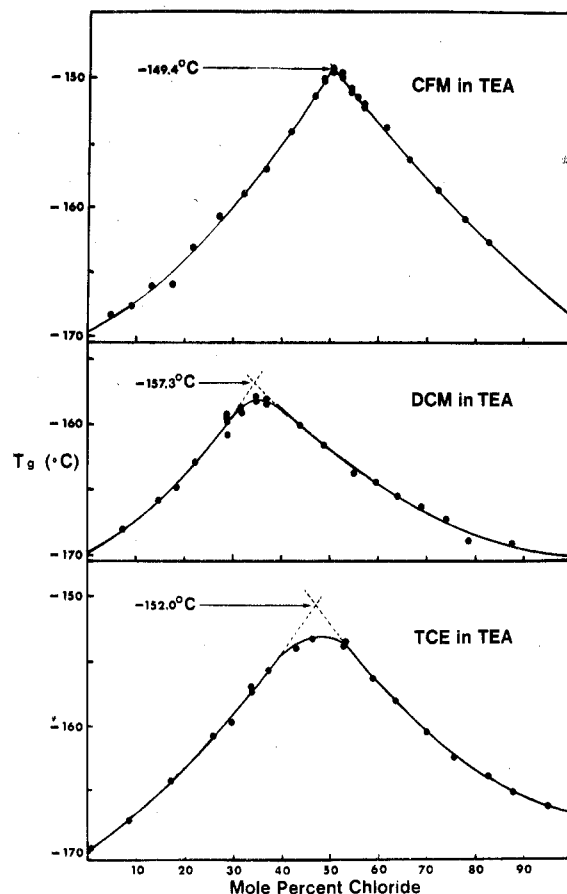


Figure 6. Mixtures of TEA with the organic chlorides: T_g as a function of composition. Arrows indicate the estimated T_g for each chloride-TEA complex.

crystallization was observed to occur only at the equimolar composition.

Figures 4-6 show representative examples of the composition dependence of T_g in the mixtures studied. In all cases but one the T_g value of the mixture lies above the value predicted by a linear composition dependence. In most mixtures this results in a well defined maximum in the T_g curve. The TEA mixtures are of particular interest. A very sharp maximum is found at 50 mol % in mixtures between this material and CFM. The maximum takes the form of a cusp in so far as the accuracy of the measurements allow it to be determined. A similar maximum is found in the DCM-TEA mixtures near 33 mol % DCM. In this case these data indicate definite rounding at the peak. The TCE-TEA mixtures display a very rounded maximum, near the 50 mol % point.

An excess glass temperature T_e may be defined as the difference between the observed T_g and that predicted assuming a linear variation of T_g with molar composition. Regularities in the data appear when this T_e is plotted against composition as in Figures 7-9. In all mixtures except that between toluene and DCM the T_e value shows a maximum. TEA and BZA mixtures have not been included in these figures. TEA attains maximum T_e values of 19, 15, and 12 °C in the CFM, TCE, and DCM mixtures, respectively. BZA shows a maximum comparable in shape to that of the other carbonyls and attains a maximum T_e of 11, 3.5, and 2 °C in the CFM, TCE, and DCM mixtures, respectively. In mixtures with each proton donor the T_e value is approximately the same for each class of base. The T_e

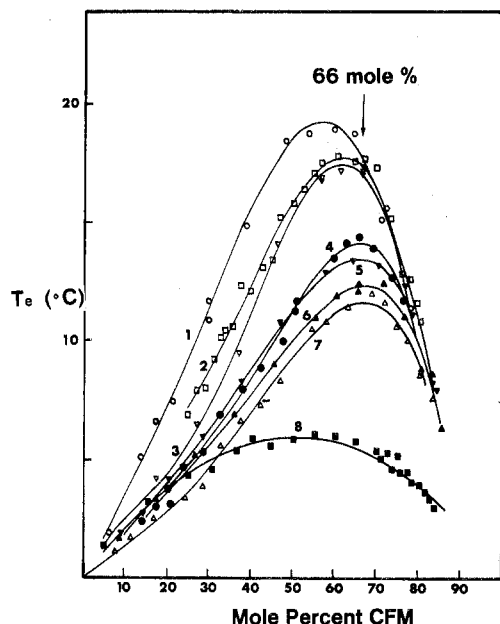


Figure 7. Excess glass temperature as a function of composition: CFM mixtures. The numeral on each curve indicates the second component of the mixture as follows: 1, DEE; 2, THF; 3, IPE; 4, acetone; 5, MEK; 6, MIK; 7, EtAc; and 8, toluene.

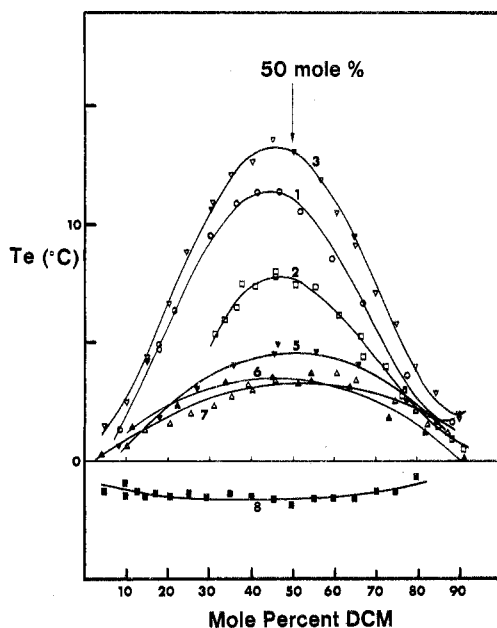


Figure 8. Excess glass temperature as a function of composition: DCM mixtures. The numeral on each curve indicates the second component of the mixture as in Figure 7.

value is greatest in size when the base is TEA or an ether. The carbonyls, including BZA and EtAc, show a generally smaller T_g value. The T_g maximum is smallest in size for toluene, and toluene in fact exhibits a T_g minimum rather than a maximum in the DCM mixtures. In the DCM mixtures (with the exception of the TEA-DCM mixture) and in the TCE mixtures the position of the T_g maximum is very nearly at the equimolar composition, while among the CFM mixtures the T_g maximum lies at almost exactly 66 mol % CFM in mixtures with the carbonyls and in the range 55–60 mol % CFM in mixtures with ethers.

Besides using the listed bases we have studied mixtures

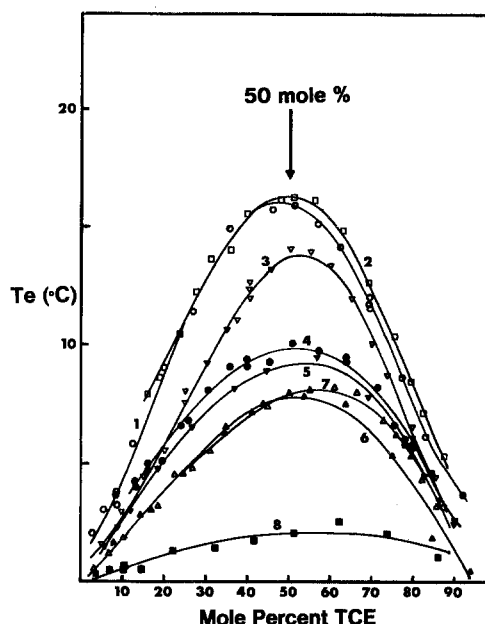


Figure 9. Excess glass temperature as a function of composition: TCE mixtures. The numeral on each curve indicates the second component of the mixture as in Figure 7.

of the organic chlorides with pyridine and cyclohexanone. We found again a broad central range of glass formation in each of these mixtures. We have not included these data in present study because we have not been able to make a reliable determination of the glass point of the pure base. We have also investigated mixtures of CFM with dimethyl sulfoxide and with *p*-dioxane. In these mixtures we observed glass formation only in a 40% molar range of composition centered on the 60 mol % CFM point.

Discussion

We believe that the maxima observed in the excess glass temperature in these mixtures are due to the formation of hydrogen-bonded association complexes between the chloride and the base. The T_g value at the maximum correlates with published values¹⁰⁻¹⁵ of the excess enthalpy of mixing at the equimolar composition. In Figure 10 this correlation is shown for the CFM mixtures; the T_g value at the maximum is found to increase more or less linearly with excess enthalpy. In these systems the major contribution to the enthalpy of mixing is believed to be the energy released upon formation of the hydrogen bond of the complex.¹⁶⁻¹⁹ The correlation therefore indicates that the T_g value increases in size with the stability of the complex. The T_g value is also found to correlate with infrared measures of base strength. The shift $\Delta\nu_s$ in the phenol O-H stretching frequency upon formation of a hydrogen bond to a particular base has been shown to correlate with base strength.²⁰ Accordingly we have plotted in Figure 11 the observed maximum T_g value for mixtures with a particular base against the base strength as measured by the $\Delta\nu_s$ for the hydrogen bond formed by that base with phenol in CCl_4 at 20 °C as tabulated by Murthy and Rao.²¹ Again we find that T_g increases with base strength and a least-squares fit of a straight line to the data points leads to a correlation coefficient greater than 0.9.

Trends in tabulated²² T_g values indicate that a positive T_g is to be expected as a result of the formation of molecular complexes. The T_g values of homologous liquids in gen-

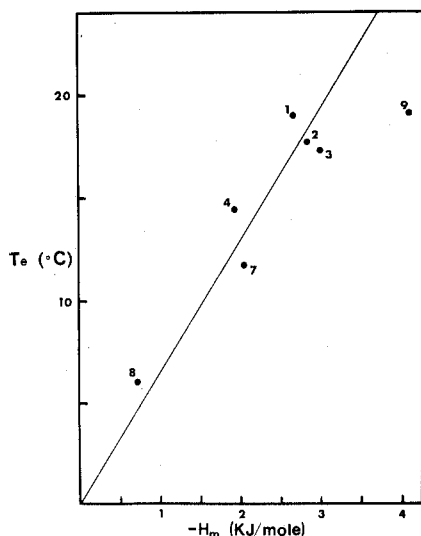


Figure 10. Peak excess glass temperature in relation to the equimolar excess enthalpy of mixing: CFM mixtures. The numeral at each point indicates the second component of the mixture as in Figure 7 (9, TEA).

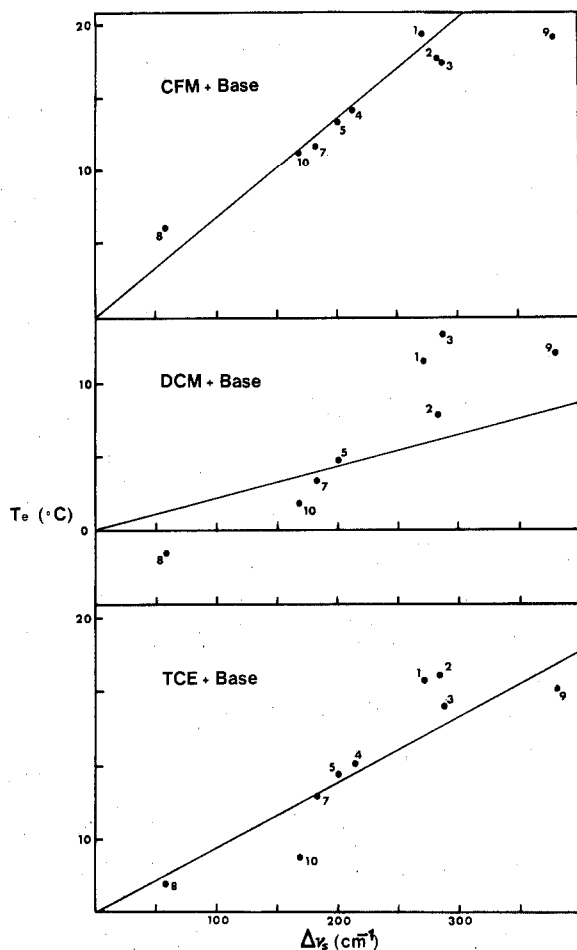


Figure 11. Peak excess glass temperature in relation to the phenol $\Delta\nu_s$ for the base. The numeral at each point indicates the base as in Figure 10 (10, BZA).

eral increase with molecular size. Since the free energy release upon formation of a complex can be shown to be large in comparison with the thermal energy at the glass point, most of the molecules in solution capable of participating

in complex formation can be expected to do so. Such complexes once formed can be expected to live a long time in comparison with the mean time between molecular collisions. The creation of larger molecular units will then have the effect of increasing T_g .

The cusp found in the T_g curve for the CFM-TEA mixtures strongly suggests that we are observing virtually complete association between CFM and TEA. That the association is in the form of a 1:1 complex is indicated by the occurrence of the cusp at the 50 mol % composition. The cusp appears because the character of the mixture changes sharply at the 50 mol % point. If association is complete the species in solution change from TEA plus complex to CFM plus complex at the 50 mol % point. The conclusion that association is virtually complete in these mixtures is supported by the NMR measurements of Wiley and Miller.²³ These authors report the enthalpy ΔH of formation of the CFM-TEA hydrogen bond to be -17.0 kJ/mol and the entropy change to be -63.6 J/mol deg at room temperature. If these values are assumed to be temperature independent, the free energy change upon bonding at the cusp temperature must be -9.1 kJ/mol implying an association constant K of 6900 (mole fraction)⁻¹ at this temperature. This K value implies that complex formation is almost 99% complete at the cusp temperature. Accordingly we believe that we are observing complete CFM-TEA association and that the cusp temperature of -149 °C represents the T_g value of the complex.

The rounding of the peak in the DCM-TEA mixtures suggests that association in these mixtures is not complete. The position of the maximum indicates the formation of a 2:1 complex representing the bonding of TEA molecule to each of the two DCM protons. The intersection points of quadratic curves fit to the two sides of the maximum lead to an estimate -157 °C as the T_g value of this complex as shown in Figure 6.

The T_g maximum in the TEA-TCE mixtures occurs at a point near 50 mol % TCE, which indicates formation of a 1:1 complex. The pronounced rounding of the maximum in these mixtures suggests that complex formation is far from completion. This conclusion is consistent with the weakness of TCE as a proton donor.^{4,5}

The fact that the carbonyls and ethers show a T_g maximum in the CFM mixtures near 60 mol % CFM suggests that the formation of a 2:1 CFM:base bicomplex is the predominant mode of association in these mixtures. The formation of such a bicomplex between CFM and acetone, in which two CFM molecules are most likely directly bonded to each acetone oxygen, has been reported by several authors.^{12,24-27} Since an ether is in general a stronger base than a carbonyl,²⁰ bicomplex formation of this type can be expected in ether mixtures as well.

Among the DCM mixtures with an oxygen carrying base, the T_g maximum occurs at the 50 mol % composition. DCM is known to be a rather strong proton donor, although weaker than CFM.²⁸ Since each oxygen atom has two proton acceptor sites, and each DCM molecule can donate two protons to a bond, chainwise association with DCM and base serving as alternate links in the chain should be possible. The bond entropy and enthalpy for the DCM-acetone bond given by Pang and Ng²⁹ imply association very nearly as extensive as in the CFM mixtures at the glass temperature. Therefore the presumed association chains should grow very long as the equimolar composition is approached. The Gibbs-DiMarzio theory of the glass transition in long

chain polymers³⁰ should describe the effect of this chain growth qualitatively.³¹ This theory predicts a steep initial rise in T_g leading to large increases in T_g as chains form from the monomer. Because the T_e values in the DCM mixtures are smaller than in the CFM mixtures where this sort of chain formation cannot occur, we doubt that chain formation occurs in the DCM mixtures. We believe that the position of the T_e peak near the equimolar composition indicates the formation of a 1:1 complex with a single DCM molecule bound to a single base. Bond angles should prevent the formation of a second hydrogen bond between the two molecules. The hydrogen atom in a bond seldom deviates far from the line connecting the two atoms bound together,³² and bond angles at the hydrogen are seldom smaller than 150°. For the two DCM protons to occupy both acceptor sites on the oxygen atom would require a C-H-O bond angle of about 71° in each bond. Further evidence that one DCM proton is free in the 1:1 complex is the fact that the T_e peak occurs at compositions slightly poorer in the DCM than 50 mol. % among the ether mixtures. This indicates a small amount of bicomplex formation with a single DCM molecule binding two ether molecules. The presence of the bicomplex shows that one DCM proton is free in the 1:1 complex to bind a second molecule.

The effect of complex formation on the glass transition is most easily understood in terms of its effect on the entropy of the mixture. There is increasing evidence^{33,34} that the occurrence of the glass transition is due to the decrease of configurational entropy associated with structural rearrangements in the liquid. Complex formation in the mixtures investigated in the present work produces negative excess entropies of mixing whose composition dependence runs generally parallel to that of the excess enthalpy of mixing. Much of the entropy loss upon formation of a complex must be configurational as the molecules associating lose the ability to move independently of each other. A further loss in configurational entropy must arise from the increase in the so-called "physical interactions"³⁵ produced by association. The materials that we are concerned with here are highly polar with electric dipole moments of the order of 1 to 2 D.³⁶ The combination of these moments can be expected to lead to a complex having a large dipole moment, which will be further increased by the dipole moment enhancement known to occur upon formation of a hydrogen bond.³⁷⁻³⁹ The increased cohesion produced by these larger dipole moments will lead to a loss of both translational and rotational freedom among the molecules of the mixture producing a loss of entropy.

The temperature at which the glass transition is observed will depend upon the rate of decrease of the remaining configurational entropy with temperature, that is, upon the liquid-glass specific heat difference ΔC_p . If association does not produce a large decrease in ΔC_p , complex formation must increase T_g . Conversely, the observed increase in T_g implies that ΔC_p must vary little with composition. This point is accessible to test, for the size of ΔC_p determines the magnitude of the DTA signature of the glass transition. Although we can make no quantitative measurements of the size of ΔC_p with our present apparatus, we observe no dramatic variation in the size of the DTA signal with composition. Further measurements to confirm the constancy ΔC_p would nevertheless be important to make.

Our results indicate that T_e correlates with the binding energy of the association complex formed in the mixture. The size of T_e implies the following order in proton donat-

ing power; CFM > TCE > DCM. We have previously found the same order in mixtures of these chlorides with the normal alcohols.⁷ The position of TCE in this series seems to be anomalous. Trew and Watkins⁴⁰ report excess enthalpies of mixing in TCE-acetone mixtures that are about one-half as great as the values given by Findlay and Kavanagh⁴¹ for DCM-acetone mixtures. The weakness of TCE as a proton donor is further shown by the lack of maximum boiling azeotropes with this material. The tabulation of Lecat⁴² lists only a single such azeotrope, that between TCE and ethylal, which boils within 1.5 °C of TCE, while the bases which give maximum boiling mixtures with DCM span a range of about 15 °C about the DCM boiling point. These data indicate that TCE is in fact a much weaker proton donor than DCM, although it shows larger T_e values. This anomaly is very difficult to explain in terms of molecular interactions. Consideration of the configurational entropy, however, suggests that the large T_e values of TCE may be due to an unusually large ΔC_p values in its mixtures. As our present data give only a very qualitative estimate of ΔC_p , it would be interesting to obtain additional calorimetric data to test this suggestion. We are grateful to the referee who suggested this possible resolution of the anomaly.

Conclusion

We have demonstrated that the formation of hydrogen bonded complexes between organic chlorides and various bases produces an increase in the glass transition temperature of the solution. For a particular chloride the T_g value increases with the strength of the bond, but the size of the increase for different chlorides and the same base is related in no obvious fashion to the bonding power of the chloride.

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Reactions of Cation Radicals of EE Systems. IV. The Kinetics and Mechanism of the Homogeneous and the Electrocatalyzed Reaction of the Cation Radical of 9,10-Diphenylanthracene with Hydrogen Sulfide¹

John F. Evans and Henry N. Blount*

Brown Chemical Laboratory, The University of Delaware, Newark, Delaware 19711 (Received October 17, 1975)

Potential step spectroelectrochemical studies of the reaction of H₂S with electrogenerated DPA^{•+} at Pt-OTE's on which PtS has been anodically formed prior to the pulsed experiment shows unusually fast consumption of cation radical during the initial stages of the pulse. Similar experiments using electrodes on which PtS has not been formed as well as those on which PtS has been formed and then cathodically discharged do not give rise to this behavior. On the basis of these experiments, it is concluded that H₂S is adsorbed onto PtS where it reacts with electrogenerated DPA^{•+} and further, that the adsorption process is kinetically slow. Open circuit relaxation spectroelectrochemical experiments of varying pulse duration show that the consumption of DPA^{•+} is initially a zero-order process involving H₂S adsorbed onto the PtS surface and, as this adsorbed material is depleted, the consumption of DPA^{•+} becomes a second-order process. In concert with the potential step experiments, these pulse time studies show the parallel nature of the heterogeneous and homogeneous reaction pathways. The zero-order rate constant for the heterogeneous process was evaluated from pulse relaxation experiments (by extrapolation to zero pulse duration) to be $1.51(\pm 0.05) \times 10^{-2} \text{ M s}^{-1}$. The bimolecular rate constant for the homogeneous process was evaluated from potential step and pulsed relaxation spectroelectrochemical measurements and stopped-flow kinetic spectrophotometry to be $6.6(\pm 1.2) \text{ M}^{-1} \text{ s}^{-1}$.

Introduction

Reactions of the cation radical derived from 9,10-diphenylanthracene (DPA), a representative EE system,² have been addressed in several recent studies in these³⁻⁶ and other⁷⁻¹² laboratories. These investigations have shown that reactions of this cation radical (DPA^{•+}) with various nucleophiles afford both addition and electron transfer products. In the course of examining the reactivity of various such "hard" and "soft" nucleophiles²² with DPA^{•+}, the reaction of this cation radical with hydrogen sulfide was investigated.

It has recently been found that the oxidation of H₂S at platinum electrodes in acetonitrile solutions gives rise to the formation of platinum sulfide surfaces on these electrodes.²³ In view of this, the mechanistic role of these anodically modified surfaces in reactions of electrogenerated DPA^{•+} with H₂S was examined. In order to clearly delineate the extent of participation of the platinum sulfide sur-

face in the reaction of DPA^{•+} with H₂S, parallel experiments utilizing stopped-flow kinetic techniques were conducted. This paper reports the results of these studies which afford the first spectroelectrochemical²⁴ observation of an electrocatalyzed reaction.

Experimental Section

The sources of and purification procedures for acetonitrile, DPA, tetraethylammonium perchlorate (TEAP), and hydrogen sulfide have already been reported.²³ The test electrodes used in this work were vapor deposited platinum optically transparent electrodes (OTE) prepared after the manner of von Benken and Kuwana²⁵ and platinum sulfide OTE's prepared by anodic oxidation of platinum OTE's as previously reported.²³ These electrodes were incorporated into an electrochemical cell of a type which has been previously described.²⁶ The potentiostat used in this work was similar in design to that reported by Pilla.²⁷ The spectroelectrochemical apparatus has also been described.²⁶