RESEARCH ARTICLE | SEPTEMBER 15 1975

# On the glass transition in organic halide–alcohol mixtures $\oslash$

Arnold V. Lesikar

Check for updates

J. Chem. Phys. 63, 2297–2302 (1975) https://doi.org/10.1063/1.431680





The Journal of Chemical Physics Special Topics Open for Submissions







# On the glass transition in organic halide-alcohol mixtures

Arnold V. Lesikar

Department of Physics, St. Cloud State University, St. Cloud, Minnesota 56301 (Received 7 May 1975)

The glass transition temperatures of binary mixtures of various aliphatic organic halides with the lower normal alcohols have been determined. For each halide a correlation is found between the alcohol glass temperature and the initial slope at the pure alcohol end of the curve of glass temperature against the mole fraction of halide. This correlation is related to the hydrogen bonding properties of the halide. For several proton donor halides a wide composition range for the glass transition is found. The excess glass temperature above that expected for an ideal mixture of these halides with the alcohols shows a maximum value of 5° or more. For some of these halides the excess glass temperature becomes negative in halide rich mixtures. These results are taken to indicate the formation of alcohol-halide clusters in alcohol rich mixtures and dissolution of hydrogen bonded alcohol aggregates in halide rich mixtures.

# INTRODUCTION

Previous work in this laboratory verified the applicability of certain expressions for the composition dependence of the glass transition in various alcohol mixtures.<sup>1</sup> The results of this study were interpreted in terms of the hydrogen bonding properties of the mixture components. Various organic halides hydrogen bond with the alcohols.<sup>2</sup> As the strength of the bond formed is quite different for different halides, organic halide-alcohol mixtures form a convenient system for studying the effect of hydrogen bonding between the components of a mixture on the process of glass formation.

## EXPERIMENTAL

All solvents used were analytical reagent grade with the exception of 1-hexanol, which was practical. A sample of 1-hexanol was prepared by fractional distillation on a 50 plate column taking the center fraction. As the distilled sample showed the same glass temperature as the undistilled material, and the same was true of its mixtures with tricholoroethylene  $C_2HCl_3$ , the 1-hexanol was used without purification for the balance of the experimental work. All solvents were supplied by the Mallinckrodt Chemical Co. with the exception of the absolute ethanol, purchased from U.S. Industrial Chemicals Co., and the tetrachloroethylene C<sub>2</sub>Cl<sub>4</sub> purchased from Matheson, Coleman, and Bell. The water content of the materials used was listed as less than 0.1% where reported on the label. The water content was not given for the alcohols other than methanol, and tests were carried out to assess the effect of water as an impurity. One percent added water was observed to produce a change of at most 1° in the glass transition temperature  $(T_{e})$  of any of the alcohols used.

Mixtures were prepared gravimetrically. The glass temperatures were determined by differential thermal analysis DTA. The DTA apparatus consists of a 260 g aluminum block heated by a nichrome heater wound on its circumference. Samples consist of about 10  $\mu$ l of materials contained in a 1 mm diam pyrex melting point capillary. The reference material used for differential temperature  $\Delta T$  measurements was either reagent grade benzene or carbon tetrachloride CCl<sub>4</sub>. Temperatures were measured by means of thermocouples formed from 0.003 in. diameter Teflon coated copper and constantan wire immersed in the sample and DTA reference material. The values of sample temperature T were determined from the record of a chart recorder driven by the output of a Hewlett Packard HP 419A dc Null voltmeter serving as the galvanometer of a Leeds and Northrup K-3 potentiometer. The thermocouple for the T measurement was referenced to liquid nitrogen temperature. The  $\Delta T$  values between sample and DTA reference material were determined from a chart recorder driven by an identical voltmeter connected directly to the  $\Delta T$ thermocouple. The T thermocouple was calibrated at the melting point of absolute methanol, and millivolts were converted to degrees in standard fashion.<sup>3</sup> The  $T_{g}$ values are taken to represent the onset of the transition determined using the procedure of Thompson.<sup>4</sup> Temperature measurements were found to be reproducible to within a standard deviation of 0.4 °C, and the absolute accuracy is estimated to be  $\pm 1.5^{\circ}$ . Because the alcohols used are hygroscopic, the pickup of water during the course of a run was estimated by test runs carried out on the methanol. Added water produces a characteristic DTA peak at the melting point of the methanol-water eutectic, <sup>5</sup> which is clearly visible with as little as 0.4%added water. The eutectic peak could not be seen in any test runs with pure methanol, and the absorption of water from the atmosphere during the course of a run is judged to be less than 0.2%.

In most of the measurements samples were vitrified by quenching them to the temperature of liquid nitrogen. They were then inserted in the DTA block which had been previously cooled to the same temperature. Quenching the sample may lead to a small peak following the transition.<sup>6</sup> Because this peak sometimes made it difficult to determine  $T_{e}$ , certain samples were rapidly cooled to a point somewhat above  $T_{e}$  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 on the block. Test measurements on material vitrified by both methods showed no difference in  $T_{e}$ .

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

TABLE I. Glass transition temperature in degrees Celsius of normal alcohols and organic halides.

Compound	T <sub>g</sub>
Methanol	$-170.5\pm0.1$
Ethanol	$-175.9 \pm 0.1$
<i>n</i> -Propanol	$-173.2\pm0.1$
<i>n</i> -Butanol	$-161.6 \pm 0.1$
<i>n</i> -Pentanol	$-152.4 \pm 0.1$
<i>n</i> -Hexanol	$-143.3\pm0.1$
Carbon Tetrachloride	$-142.6\pm0.9$
Chloroform	$-167.7 \pm 0.3$
Dichloromethane	$-171.0 \pm 0.2$
Trichloroethylene	$-166.1\pm0.2$
Tetrachloroethylene	•••
1, 2-Dichloroethane	•••

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.

DTA measurements were carried out at a heating rate of 12° per minute. The pure solvents used are given in Table I together with their  $T_g$  values. The alcohols can be vitrified as pure materials, and the values listed were determined as the mean of many direct measurements on the vitreous materials. None of the organic halides can be vitrified except in mixtures, and the values listed were determined by extrapolation. In each case mixtures were chosen to allow as close an approach to the pure halide as possible, and a quadratic extrapolation in mole percent was made. The value for  $C_2HCl_3$  is the mean result for mixtures with four different alcohols and with diethyl ether. The value for dichloromethane  $(CH_2Cl_2)$  is the mean result for mixtures with ether. toluene, and benzyl alcohol. In each case the glass transition can be traced to within 90 mol% of the pure halide with these compounds. The value for chloroform  $(CHCl_3)$  is the mean result for mixtures with toluene or benzyl alcohol and involved an extrapolation from 80 mol% CHCl<sub>3</sub>. The CCl<sub>4</sub> value is the result of an extrapolation from  $68 \mod \%$  in a mixture with 2-octanol. All components of the mixtures used in these extrapolations were analytical reagent with the exception of the 2-octanol which was practical. A 2-octanol sample was prepared by fractional distillation, taking the central onethird boiling between 180° and 181°. The other materials used in these determinations were used without further purification. The errors assigned to these values are statistical only. The CCl<sub>4</sub> value is accepted in spite of the large range over which the extrapolation is made because it agrees with the value previously determined using a different method of extrapolation.<sup>1</sup> Further, interactions between the alcohol and CCl<sub>4</sub> should be sufficiently small that  $T_g$  will vary smoothly with composition. No mixtures were found for the remaining halides with a sufficiently wide range of glass formation to permit an extrapolation.

# RESULTS

The organic halides show a fascinating variety in their behavior as components of glass forming mixtures. The variation in the composition range of glass formation is very great. The widest range of glass formation is shown by  $C_2HCl_3$ ; the glass transition can be followed to 90 mol% halide in most of the mixtures studied before crystallization intervenes. For CHCl<sub>3</sub> and CCl<sub>4</sub> the range of glass formation is somewhat narrower, while in C<sub>2</sub>Cl<sub>4</sub> mixtures the transition cannot be followed beyond 30 mol% halide. The range of glass formation in CH<sub>2</sub>Cl<sub>2</sub> mixtures is somewhat narrower than in CHCl<sub>3</sub> mixtures. Normally the range of glass formation is terminated by the onset of crystallization. However in the mixtures between  $CH_2Cl_2$  and the normal alcohols heavier than ethanol, the glass transition splits into two transitions separated in temperature as the percent of CH<sub>2</sub>Cl<sub>2</sub> is increased. The onset of this phenomenon occurs at about 50 mol% halide in *n*-butanol mixtures. As halide is added these transitions remain fixed in temperature. A similar double transition is seen in mixtures with 1, 2-dichloroethane  $(C_2H_4Cl_2)$ . A cloudy glass quite different in appearance from either crystalline material or the normal vitrified solvent is formed in these mixtures. The liquid resulting from the softening of the glass has the appearance of an emulsion. Our conjecture is that these solutions separate into two liquid phases as they are cooled.

The dependence of  $T_{e}$  on composition also shows wide variation among these mixtures. Figure 1 shows the variation of  $T_{e}$  in representative CCl<sub>4</sub> mixtures and C<sub>2</sub>Cl<sub>4</sub> mixtures. The variation of  $T_{e}$  in CCl<sub>4</sub> mixtures is monotonic as far as the transition can be traced except in the case of mixtures between CCl<sub>4</sub> and *n*-hexanol. Here the glass temperatures of the pure components are very nearly identical, and a gentle maximum is seen in the  $T_{e}$  curve. The transition in the corresponding C<sub>2</sub>Cl<sub>4</sub>



FIG. 1. Glass transition temperature in relation to composition:  $CCl_4$  and  $C_2Cl_4$  in *n*-hexanol and in *n*-propanol.



FIG. 2. Glass transition temperature in relation to composition:  $CHCl_3$  and  $C_2HCl_3$  in *n*-butanol mixtures.

mixture parallels that in the  $CCl_4$  mixture but at a somewhat lower temperature.

Figures 2 and 3 show the  $T_s$  variation in representative CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> mixtures and in typical CH<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> mixtures. These materials show well defined maxima in the  $T_s$  curves as far as the glass transition can be followed. In corresponding mixtures the maximum is greatest for CHCl<sub>3</sub> and smallest for CH<sub>2</sub>Cl<sub>2</sub>.

#### **INITIAL MOLAR SLOPES**

The initial slope in the molar composition dependence of  $T_g$  at pure alcohol was determined for all the mixtures studied. This slope reflects the effect of the first halide molecules added and should be sensitive to the halide-alcohol interaction independent of interactions among the halide molecules. Initial slopes in all the mixtures except those of chloroform were derived by fitting polynomial functions to the data over the entire range of composition. In each case the lowest order polynomial that would fit the data to within a standard deviation of  $0.4^{\circ}$  was used. In a few cases a fit this good could not be obtained, and the polynomial giving the minimum over-all standard deviation was used. In no case was a polynomial of higher order than the sixth used, nor was the standard deviation more than one degree. The initial slopes in these fits is given by the linear term of the polynomial. Because the CHCl<sub>3</sub> mixtures show a rise to the maximum that is very nearly linear, the initial slopes in these mixtures were derived by fitting a straight line to the data over the range of composition from zero to approximately 35 mol% CHCl<sub>3</sub>. As measured by the standard deviation of the fit these fits are as good as the polynomial fits made to the other mixtures.

Our earlier work<sup>1</sup> had shown a correlation between the curvature of the  $T_g$ -composition graph and the difference in  $T_g$  values of the components. This suggested that a correlation might exist between the initial slope and the  $T_g$  of the alcohol in the present case. The correlation found is shown in Fig. 4. The correlation fits a straight line well to all cases. The two lightest alcohols, metha-

nol and ethanol, are in almost every case the only alcohols which deviate. The straight lines shown in the figure are the result of a least squares fit to the data for the four alcohols heavier than ethanol. The parameters of these lines are given in Table II.

#### EXCESS GLASS TEMPERATURES

Gordon and Taylor derived an expression<sup>7</sup> for the dependence of  $T_g$  on composition in polymer mixtures. These authors based their derivation on the continuity of the specific volume at the glass transition. This together with the assumption of an ideal mixture, in the sense that there is no excess volume of mixing, leads to a representation of  $T_g$  for a mixture as weighted average of the  $T_g$  values of the pure components:

$$T_{g} = \frac{A_{1}(1-x)T_{g1} + A_{2}xT_{g2}}{A_{1}(1-x) + A_{2}x} , \qquad (1)$$

where x is the mole fraction of component 2. The weighting factors  $A_1$  and  $A_2$  are the differences  $\Delta\beta_1$  and  $\Delta\beta_2$  in the temperature derivative of the volume between liquid and glass for the two components, respectively. Gordon and Taylor were concerned with dilatometric determinations of  $T_{\varepsilon}$ ; for DTA a derivation based on the continuity of the enthalpy at the glass transition is more appropriate. For ideal mixtures, without enthalpy of mixing, a  $T_{\varepsilon}$ -composition dependence of the Gordon-Taylor form is found with the liquid-glass specific heat difference  $\Delta c_p$  serving as the weighting factor of each component. This function predicts an initial molar slope of the form

$$dT_{g}/dx = A_{g}/A_{1}(T_{g2} - T_{g1}) .$$
<sup>(2)</sup>

We have taken the Gordon-Taylor function (1) to rep-



FIG. 3. Glass transition temperature in relation to composition:  $CH_2Cl_2$  and  $C_2H_4Cl_2$  in *n*-propanol mixtures.



FIG. 4. Initial molar slopes of organic halide mixtures in relation to  $T_{\varepsilon}$  of the alcohol component.

resent the  $T_g$  variation in an ideal mixture. Excess glass temperatures  $T_e$ , in analogy to the excess thermodynamic quantities, may be determined by subtracting the Gordon-Taylor glass temperature from the observed  $T_{\rm g}$ . In this calculation the weighting factor ratio  $A_2/A_1$ was determined from the initial molar slope by (2). Since the weighting factor ratio is near one, the  $T_e$  values found lie within one degree of those derived by assuming that  $T_{s}$  for an ideal mixture is a simple linear function of the halide mole fraction x. Such  $T_e$  values are shown in Figs. 5, 6, and 7 for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub> respectively. The  $T_e$  values in each set of mixtures show little variation, decreasing only slightly in size from npropanol to n-hexanol. The  $T_e$  values are positive and largest in size in the CHCl<sub>3</sub> mixtures. The values are somewhat smaller in the  $C_2HCl_3$  mixtures and a sign change is observed in the halide rich region in mixtures with the hexanol. The smallest  $T_e$  values are seen in the CH<sub>2</sub>Cl<sub>2</sub> mixtures. Although the curves cannot be traced into the halide rich region their appearance suggests that  $T_e$  would become negative if the  $T_e$  values could be followed this far.

#### DISCUSSION

The chlorine atoms of the organic halides studied here are known to activate the hydrogen atoms of the molecule to hydrogen bond formation.<sup>8</sup> The values observed for the excess glass temperature  $T_e$  correlate with the strength of the interaction between halide and alcohol. The largest positive  $T_e$  values are found in the mixtures with CHCl<sub>3</sub>, which is the strongest proton donor of the halides studied here.<sup>8,9,10</sup> In the CCl<sub>4</sub> mixtures  $T_e$  is

TABLE II. Parameters of the straight lines fit in Fig. 4.

Compound	Slope	T intercept (°C
CCl4	$2.44 \pm 0.09$	$-139 \pm 8$
C <sub>2</sub> Cl <sub>4</sub>	$1.47 \pm 0.16$	$-131 \pm 21$
CHCl <sub>3</sub>	$1.29 \pm 0.05$	$-139\pm8$
C <sub>2</sub> HCl <sub>3</sub>	$1.21 \pm 0.20$	$-140 \pm 35$
CH <sub>2</sub> Cl <sub>2</sub>	$1.13 \pm 0.13$	$-139 \pm 24$
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	$1.63 \pm 0.21$	$-147 \pm 27$



FIG. 5. Excess glass temperature in relation to composition:  $CHCl_3$  in *n*-proponal, *n*-butanol, and *n*-hexanol.

very small, attaining a maximum value of about 2°. The CCl<sub>4</sub> cannot act as a proton donor, and there remains only only a very weak attractive interaction of the order of 10 cal/mole between a hydroxyl oxygen and a chlorine of the CCl<sub>4</sub>.<sup>11</sup> The size of  $T_e$  indicates that the halide-alcohol interaction at temperatures in the vicinity of the glass point decreases in the order CHCl<sub>3</sub> > C<sub>2</sub>HCl<sub>3</sub> > CH<sub>2</sub>Cl<sub>2</sub> > CCl<sub>4</sub>.

The variation of  $T_e$  with composition parallels the composition dependence of the enthalpy of mixing of the liquids. This composition dependence reflects a competition between hydrogen bonding of the halide molecule to groups of alcohol molecules and a disruption of the hydrogen bonding among alcohol molecules by dilution.<sup>11</sup> At low halide concentration, hydrogen bonding of the halide prevails, leading to negative excess enthalpies of mixing; while at higher halide concentrations the dilution effect is dominant, producing positive excess enthalpies. The same competition should determine the composition dependence of  $T_g$ . The value of  $T_g$  can be expected to increase with the size of hydrogen bonded aggregates present in the liquid.<sup>12</sup> Formation of larger aggregates



FIG. 6. Excess glass temperature in relation to composition:  $C_2HCl_3$  in *n*-propanol, *n*-butanol, and *n*-hexanol.



FIG. 7. Excess glass temperature in relation to composition:  $CH_2Cl_2$  in *n*-propanol, *n*-butanol, and *n*-hexanol.

by the bonding of halide molecules then leads to an increase in  $T_{\mathfrak{g}}$  at low halide concentrations; while the disruption of alcohol aggregates by dilution at high halide concentration produces the opposite effect.

The increase in the width of the range of negative  $T_e$ from CHCl<sub>3</sub> to CH<sub>2</sub>Cl<sub>2</sub> is indicative of the same order of donor strength as the size of  $T_e$ . With the weaker proton donors, relatively few halide molecules are bonded to the alcohol molecules, and the dilution effect is dominant until the solution is quite rich in alcohol. The weaker the donor is the wider will be the composition range over which hydrogen bond rupture will predominate.

The failure of  $T_e$  to change sign in the CHCl<sub>3</sub> mixtures indicates that the hydrogen bonding to the available alcohol molecules is almost complete over the entire composition range. This result is consistent with the available high temperature data. Tabulated equilibrium constants K for bonding between CHCl<sub>3</sub> and a carbonyl or ether oxygen<sup>13</sup> are of the order of 2(mole fraction)<sup>-1</sup>. The enthalpy decrease  $\Delta H$  on bond formation is about 3000 cal/mole. Bonding to a hydroxyl oxygen can be expected to yield similar values. The equilibrium constant gives a free energy décrease  $\Delta F$  of about 300 cal/mole at room temperature, corresponding to an entropy contribution  $T \Delta S$  of 2700 cal/mole. At  $T_{g}$  the entropy contribution to the free energy change would be about half as great, giving a  $\Delta F$  of about 1600 cal/mole upon formation of bond. The thermal energy  $RT_r$  of about 250 cal/mole is not therefore sufficient to disrupt any appreciable fraction of the CHCl<sub>3</sub>-alcohol bonds. Since a sizeable fraction of  $C_2HCl_3$  molecules do not bond, the  $\Delta F$  for this material must be of the order of 250 cal/mole at the temperatures in question.

The correlation observed in the initial molar slope suggests that the bonding of a halide molecule to an alcohol group produces an aggregate having a fairly well defined  $T_g$  value. In the absence of interactions among the components of a mixture the  $T_g$  should be an appropriately defined average of the  $T_g$  values of the components. Although no fundamental relation can be derived without a detailed understanding of the relaxation mechanisms prevailing in the mixture, <sup>14</sup> an approximately linear relationship can be expected.<sup>15</sup> This would lead to an initial molar slope proportional to the difference in the  $T_{\rm g}$  values of the components, as is given by Eq. (2). If there were no interaction between a halide and an alcohol, a plot of the value of the initial molar slope for a given halide against the  $T_{g}$  of the alcohol through the series of alcohols should show an intercept on the  $T_g$ axis at the halide  $T_g$ . In fact, the alcohol-halide interaction is weak when the halide is CCl<sub>4</sub>, and the value observed for the  $T_g$  intercept is only 4° higher than the  $T_g$ of  $CCl_4$ . However, the intercepts observed for  $CHCl_3$ ,  $C_2HCl_3$  and  $CH_2Cl_2$  lie about 30° higher than the extrapolated  $T_{r}$  for the pure halide in each case. This suggests that the second component in these mixtures is not the isolated halide molecule, but rather a fairly well defined halide-alcohol aggregate, which would show a high  $T_{r}$  if it could be prepared in isolation. Scatchard and Raymond<sup>16</sup> have suggested that the presence of a chloroform molecule in a hydrogen-bonded cluster of alcohol molecules increases the number of alcohol molecules in the cluster. In the light of this suggestion it would be reasonable to view the alcohol-halide mixture as a mixture between clusters of alcohol molecules lacking a halide member and showing the  $T_g$  of the pure alcohol, and larger clusters, having a halide member, and showing a higher  $T_g$  value because of their larger size. The  $T_g$ intercept observed should then approximately represent the  $T_{r}$  value of a mixture in which all the molecular clusters were the larger clusters of the second type. The larger clusters need not have a definite stoichiometry; it is merely necessary that the average size be greater than that of the clusters without a halide member.

Our results are anomalous in the strength of the interaction attributed to CH<sub>2</sub>Cl<sub>2</sub>. Measurements of the enthalpy of mixing of this material with various proton acceptors indicate that its power as a proton donor exceeds that of C2HCl3. The fact that CH2Cl2 has two active protons suggests that the glass temperatures of its mixtures with the alcohols may not be directly comparable with those of  $C_2HCl_3$ . Since each  $CH_2Cl_2$  molecule can bind to two alcohol molecules, CH<sub>2</sub>Cl<sub>2</sub> can be expected to break up alcohol association polymers more easily by occupying proton acceptor sites. If the CH<sub>2</sub>Cl<sub>2</sub>-alcohol bonding at high halide concentrations leads primarily to small cyclic polymers rather than chainwise association, the CH<sub>2</sub>Cl<sub>2</sub> will reduce the average aggregate size even at concentrations low enough in the halide that mutual bonding among the alcohols continues to play an important role. This reduction in the average size of the aggregate will then have the effect of reducing  $T_e$  and  $T_e$ . At very low halide concentrations, the two protons of CH<sub>2</sub>Cl<sub>2</sub> can be expected to

cross link aggregates leading to an increase in cluster size at least as great as that of the other halides, thereby producing clusters having a high  $T_g$  in the manner discussed in the preceding paragraph.

## CONCLUSION

The present work correlates with other work demonstrating the importance of the hydrogen bond in determining the glass temperature of a material.<sup>12,17</sup> The excess glass temperatures observed clearly demonstrate the effect of halide-alcohol association. The initial molar slopes suggest the existence of more or less well defined halide-alcohol aggregates at least at low halide concentration. Whether these aggregates deserve the name "complex" is questionable in view of the fact that no definite stoichiometric relationship has been demonstrated. Clearly, however, the glass transition is very sensitive to the degree of association of the components of the mixture and serves as a useful tool to probe complex formation in solution.<sup>18</sup>

#### ACKNOWLEDGMENT

The author wishes to acknowledge with gratitude the support of both the Physics department and the Chemistry department of St. Cloud State University and their respective chairmen, Dr. Philip Youngner and Dr. John Carpenter.

- <sup>1</sup>A. V. Lesikar, Phys. Chem. Glasses (to be published).
- <sup>2</sup>G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (Freeman, San Francisco, 1960).
- <sup>3</sup>R. C. Weast, Ed., *Handbook of Chemistry and Physics*, 48th ed. (Chemical Rubber, Cleveland, 1967), p. E 91.
- <sup>4</sup>E. V. Thompson, J. Polym. Sci. A 4, 199 (1966).
- ${}^{5}$ G. A. Miller and D. K. Carpenter, J. Chem. Eng. Data 9, 371 (1964).
- <sup>6</sup>W. Wrasidlo, Adv. Polym. Sci. 13, 3 (1974).
- <sup>7</sup>M. Gordon and J. S. Taylor, J. Appl. Chem. 2, 493 (1952).
- <sup>8</sup>R. H. Ewell and L. M. Welch, J. Am. Chem. Soc. 43, 2475 (1941).
- <sup>9</sup>C. S. Marvel, F. C. Dietz, and M. J. Copley, J. Am. Chem. Soc. 42, 2273 (1940).
- <sup>10</sup>C. S. Marvel, M. J. Copley, and E. Ginsberg, J. Am. Chem. Soc. **42**, 3109 (1940).
- <sup>11</sup>J. A. Barker, J. Chem. Phys. 20, 1525 (1925).
- <sup>12</sup>E. J. Sutter and C. A. Angell, J. Phys. Chem. 75, 1826 (1971).
- <sup>13</sup>A. S. N. Murphy and C. N. R. Rao, Appl. Spectrosc. Rev. 2, 69 (1968).
- <sup>14</sup>M. Goldstein, J. Chem. Phys. 51, 3728 (1960).
- <sup>15</sup>C. T. Moynihan, A. J. Easteal, J. Wilder, and J. Tucker, J. Phys. Chem. 78, 2673 (1974).
- <sup>16</sup>G. Scatchard and C. L. Raymond, J. Am. Chem. Soc., 60, 1278 (1938).
- <sup>17</sup>E. J. Sare, C. T. Moynihan, and C. A. Angell, J. Phys. Chem. 77, 1869 (1973).
- <sup>18</sup>A. J. Easteal, E. J. Sare, C. T. Moynihan, and C. A. Angell, J. Solut. Chem. 3, 807 (1974).