On the Self-association of the Normal Alcohols and the Glass Transition in Alcohol–Alcohol Solutions

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The glass-transition temperature (T_g) in mutual binary mixtures of the primary alkanols from methanol through n-octanol has been measured as a function of composition. For mixtures of the alkanols heavier than ethanol, T_g is found to be a linear function of the number-average molecular length. Methanol and ethanol mixtures show higher T_g values than indicated by this relation. These results are found to be consistent with association of the heavier alkanols into chains of very great length in the supercooled liquid, while ethanol and methanol must form networks with a moderate degree of cross-linking between chains.

1. INTRODUCTION

The present work is part of a series of studies[1–4] using the glass transition as a tool to probe molecular interactions. Since the self-association of the aliphatic alcohols is a subject of great interest to workers in very many fields,[5,6] it is of interest to see what information glass studies can furnish about this question. Our most recent results[4] on alcohol-base mixtures suggest predominantly chainlike self-association of the supercooled liquid, while MeOH and EtOH show evidence for the formation of a crosslinked network. It was decided to investigate binary mixtures of the normal alcohols among themselves to see if our model of alcohol self-association would be consistent with the composition dependence of the glass transition. One of the most striking results of the previous study was that the initial molar slope (IMS) at the pure alcohol end of the curve of glass temperature T_g against mole fraction of added base was subject to a congruence principle[7]

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whereby the IMS of a base in a binary mixture of the normal alcohols was found to be determined by the number-average length of the alkane backbone of the alcohols. These results led us to test whether the T_g of a binary alcohol mixture might also be subject to such a congruence principle.

2. EXPERIMENTAL

The eight lowest normal aliphatic alcohols from methanol through n-octanol were chosen for study. The sources, grades, and T_g values of these materials are listed in Table I. All materials were used as received. Mixtures were prepared and T_g values were determined by differential thermal analysis (DTA) in the fashion previously described.[4]

3. RESULTS

Mixtures of all pairs of alcohols from MeOH through n-OctOH were studied. As is well known, the six lightest of these alcohols are easily vitrified,[1,2,4,8,9] and the glass transition could be followed through the entire composition range of the mixtures of these six alcohols with each other. These results are shown in Fig. 1. Figure 2 shows the T_g values for mixtures of MeOH with n-HxOH, n-AmOH, n-BuOH, n-PrOH, and n-EtOH. We found that we could not vitrify n-HptOH and n-OctOH, as other workers have also reported,[9] nor was any glass-forming range found in a series of mixtures of n-HptOH with n-OctOH. In mixtures of these alcohols with the lighter ones, the glass-forming range was terminated by the onset of crystallization as the glass transition was traced from the lighter alcohol toward compositions richer in the heavier one. Mixtures of n-HptOH showed a wider glass-forming range in general than mixtures of n-OctOH with the same alcohol.

Table I. Sources and T_g Values of Alcohols

| Alcohol	Manufacturers	Grade	T_g (°C)
Methanol (MeOH)	Baker, Mallinckrodt	Reagent	−170.4
Ethanol (EtOH)	Publicker Industries	"200 proof"	−176.1
n-Propanol (n-PrOH)	Mallinckrodt	Reagent	−173.3
n-Butanol (n-BuOH)	Baker, Mallinckrodt	Reagent	−161.5
n-Pentanol (n-AmOH)	Mallinckrodt	Reagent	−152.2
n-Hexanol (n-HxOH)	Eastman	Practical	−143.3
n-Heptanol (n-HptOH)	MCB	Chromatoquality	−132.0
n-Octanol (n-OctOH)	Baker	Reagent	−123.5
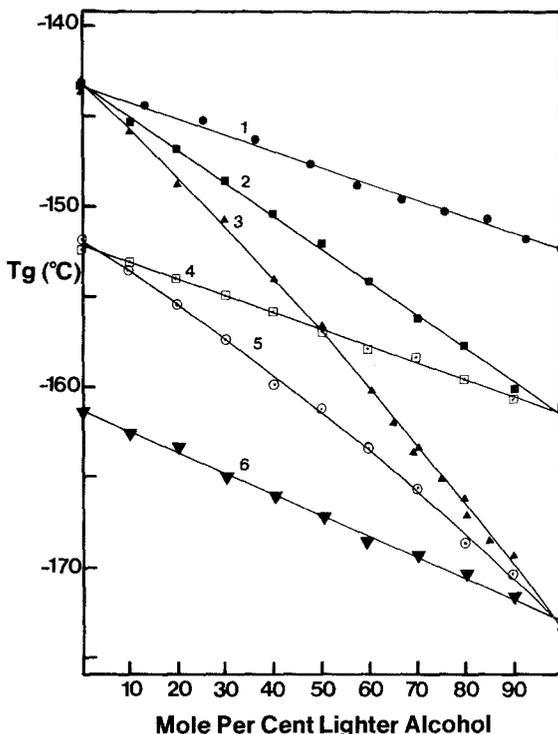
Fig. 1. Glass-transition temperature as a function of molar composition. The numbered curves represent the following mixtures: (1) *n*-HxOH in *n*-AmOH; (2) *n*-HxOH in *n*-BuOH; (3) *n*-HxOH in *n*-PrOH; (4) *n*-AmOH in *n*-BuOH; (5) *n*-AmOH in *n*-PrOH; (6) *n*-BuOH in *n*-PrOH.

As the end of the glass-forming range was approached, an exothermic peak apparently associated with crystallization of the supercooled liquid tended to merge into the glass transition. At the apparent end of the glass-forming range there was a rapid decrease in the size of the glass transition and a marked increase in the area of the endothermic melting peak in relation to the exothermic peaks in the DTA record. We found it difficult to locate the end of the glass-forming range by visual inspection of the sample, as the first evidence of crystal formation apparent to the naked eye was found at compositions much richer in the heavy alcohols than those at which the DTA signature of the glass transition disappeared. With mixtures of *n*-HptOH and *n*-OctOH in MeOH and EtOH, crystallization ensues very rapidly after the glass transition in the DTA record. As we are not confident of the range of formation of a homogeneous glass in the MeOH and EtOH mixtures with *n*-HptOH or of EtOH with *n*-OctOH, we have chosen not to
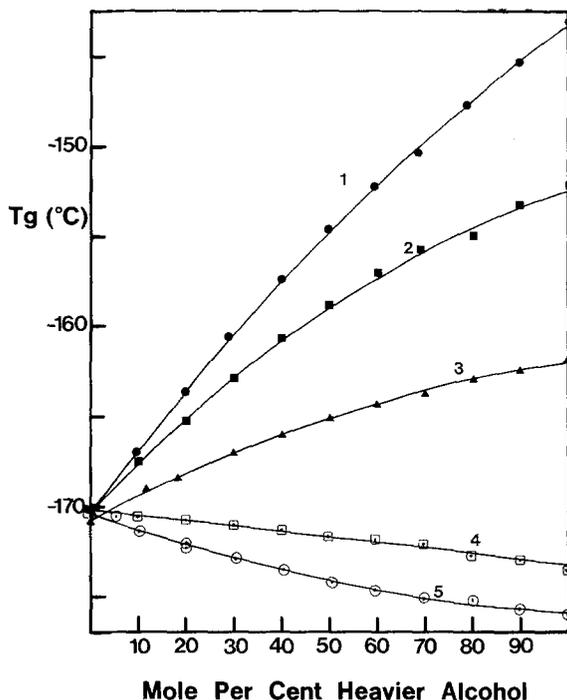
Fig. 2. Glass-transition temperature as a function of molar composition for MeOH mixtures. The numbered curves represent mixtures with the following alcohols as the second component: (1) n-HxOH; (2) n-AmOH; (3) n-BuOH; (4) n-PrOH; (5) EtOH.

include these data. We are certain, however, that the glass-forming range in MeOH–n-OctOH mixtures does not extend to compositions richer than 5 mole % in n-OctOH.

The composition dependence of T_g is very nearly linear in all mixtures. Excess glass temperatures T_e (defined as the difference between the measured T_g and the T_g predicted from a linear composition dependence) are small in all cases, usually less than 2.5°C in size. All T_e values are positive with the exception of MeOH in EtOH ($T_e = -1.0°$ at 50 mole % MeOH) and with the possible exception of the mixtures of n-BuOH in n-OctOH, where extrapolation of the measured T_g composition dependence would suggest a negative T_e of some degrees. Nonzero T_e values are found only when there is a substantial difference in the length of the alkane backbone of the alcohols mixed. Thus, the mixtures of n-HxOH with n-AmOH or n-BuOH, of n-AmOH with n-BuOH, and of n-BuOH with n-PrOH all show a composition dependence of T_g that is linear within experimental error. In view of this fact it seemed likely that the composition dependence of T_g also would be linear
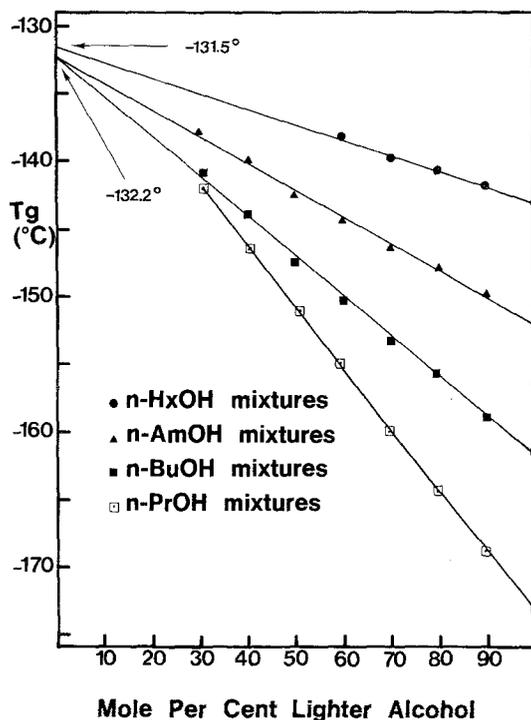
Fig. 3. Glass-transition temperature as a function of molar composition for *n*-HptOH mixtures. Extrapolated T_g values of pure *n*-HptOH are marked with arrows.

in mixtures of *n*-HptOH or *n*-OctOH with the heavier alcohols studied. We took advantage of this possibility to determine the T_g values of *n*-HptOH and *n*-OctOH by extrapolation. We find that the T_g values of *n*-HptOH determined by linear extrapolation in mixtures of *n*-HptOH with *n*-HxOH, *n*-AmOH, or *n*-BuOH agree to within better than 1°C (Fig. 3), and the average of these three values is the value we report in Table I. A similar extrapolation in mixtures of *n*-OctOH with *n*-HxOH or *n*-AmOH leads to estimates of the *n*-OctOH T_g agreeing to within 0.5°C (Fig. 4). The mean of these two estimates is the value we report in Table I. A similar extrapolation carried out in *n*-OctOH mixtures with *n*-BuOH leads to a substantially lower T_g estimate for *n*-OctOH. We reject this estimate since the larger difference in the chain length of the alcohols involved in the extrapolation makes it likely that the composition dependence of T_g is not precisely linear in this case.

In order to test the applicability of a congruence principle to these data, we have plotted the T_g values for the various mixtures against the average
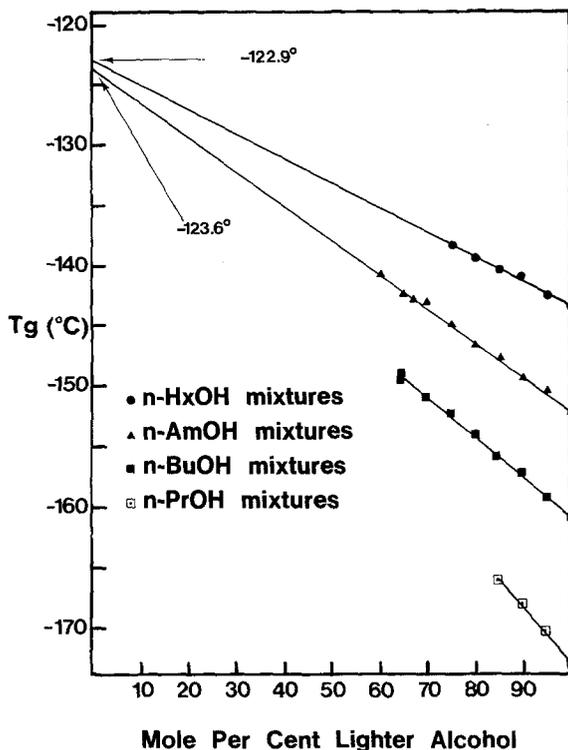
Fig. 4. Glass-transition temperature as a function of molar composition for *n*-OctOH
mixtures. Extrapolated T_g values of pure *n*-OctOH are marked with arrows.

number of carbons in the alkyl backbone. These data are displayed in Figs.
5 to 9. The mixtures of the heavier alcohols (from *n*-PrOH on) show a T_g
value linearly increasing with the average number *n* of carbon atoms in the
backbone. A least-squares fit to these data yields the line

$$T_g \, (°C) = -201.8 + 9.9n \tag{1}$$

The measured T_g values scatter about the fitted line with a standard devia-
tion of 0.7°C. MeOH and EtOH and their mixtures show T_g values consistently
higher than those given by this fit (Fig. 9).

In order to further test the applicability of the congruence principle, we
have prepared a series of binary alcohol mixtures having integral average
carbon number. We have compared the measured T_g values of these mixtures
with the T_g found for the pure alcohol having the same backbone length.
These data are presented in Table II. In all cases but one the agreement be-
tween the T_g value of the mixture and that of the pure alcohol is within 1°C.
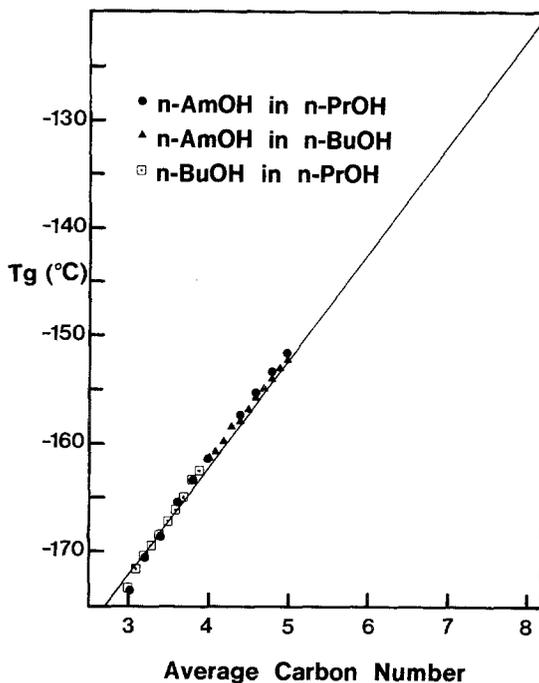The single deviant mixture (33 mole % *n*-BuOH in *n*-HptOH) is very near

Fig. 5. Glass-transition temperature as a function of number-average length of the alkyl backbone in *n*-AmOH and *n*-BuOH mixtures. The straight line is drawn according to Eq. (1).

the end of the glass-forming range of the *n*-BuOH mixtures with *n*-HptOH. We conclude therefore that the T_g values of the normal alkanols from *n*-PrOH to *n*-OctOH obey a congruence principle to an accuracy better than 1°C.

4. DISCUSSION

In our previous work[4] we cited evidence that the normal alcohols in the supercooled liquid associate into hydrogen-bonded chains of great length. Each polymeric associate is a chain of hydroxyl groups O–H . . . O–H . . . O–H . . . held together by hydrogen bonds with the alkyl backbones of the individual molecules serving as side chains. The glass transition in such a polymerically associated liquid should be described by the Gibbs–DiMarzio theory of glass formation.[10] If the length of the polymeric associates is very great, the value of T_g will be determined mainly by the average bond flex energy $\Delta\varepsilon$.[11] The value of $\Delta\varepsilon$ must be a suitable average of the values
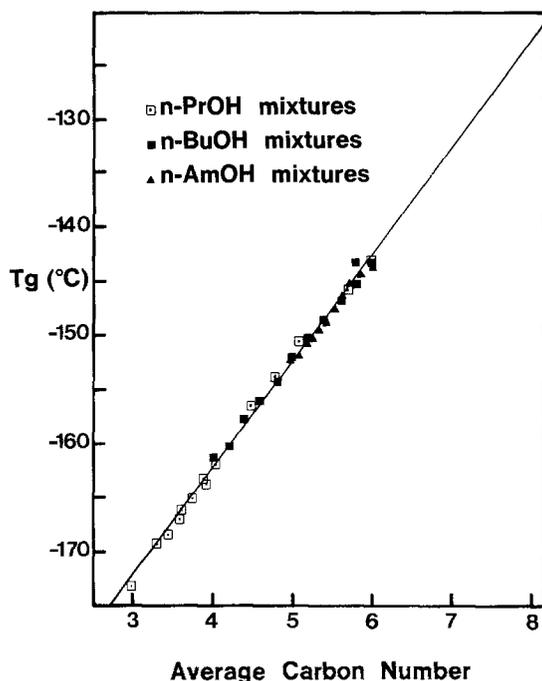
Fig. 6. Glass-transition temperature as a function of number-average length of the alkyl backbone in n-HxOH mixtures. The straight line is drawn according to Eq. (1).

appropriate to the different bonds present in the associates.[11] The effective $\Delta\varepsilon$ will then be an average of the values appropriate to the rather stiff co-valent bonds forming the backbone of each alcohol molecule and the rela-tively flexible hydrogen bonds joining adjacent molecules in the association chain. The large difference in flexibility between the hydrogen bonds and the covalent bonds makes it unlikely that the average bond energy can be com-puted as a simple arithmetic average over the total number of bonds.[11]

This picture of the glass transition accounts for the congruence principle we have observed. The average flex energy will depend upon the ratio of the number of covalent bonds to the number of hydrogen bonds in the associa-tion polymers. As the length of the alkyl backbone increases, the fraction of covalent bonds in each associate will increase. The average flex energy will increase as a result, and a higher T_g will be found. If we assume that there is no interaction between neighboring bonds, the average flex energy will depend only upon the ratio of the total number of covalent bonds in each associate to the total number of hydrogen bonds. It will be immaterial whether the molecules making up the associate are identical or not; it will be the number-average length of the molecule which determines T_g.
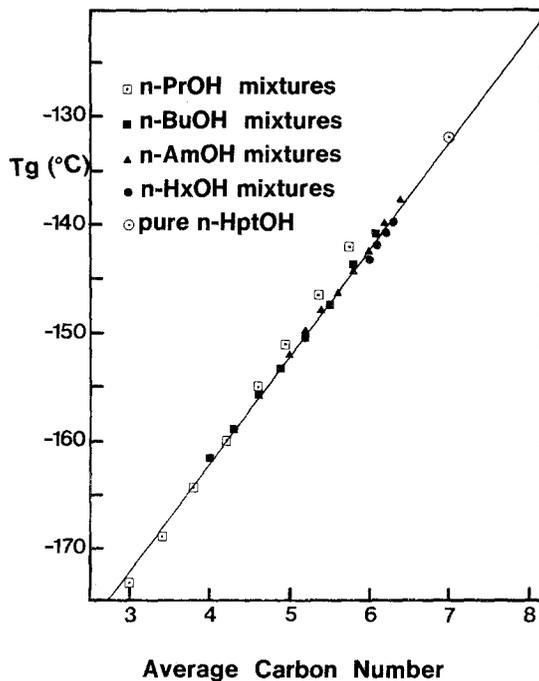
Fig. 7. Glass-transition temperature as a function of number-average length of the alkyl backbone in n-HptOH mixtures. The straight line is drawn according to Eq. (1).

We can use our results to estimate the flex energy of the O–H...O hydrogen bond. The $n = 0$ intercept of T_g from Eq. (1) should represent the T_g values of a chain of hydrogen-bonded hydroxyl groups showing the same type and degree of association as a heavy alcohol, but lacking the side chains formed by the alkyl backbones of the molecules. Using this value together with the relation [11]

$$T_g = 0.521 \, \Delta\varepsilon/k \qquad (2)$$

yields the value $\Delta\varepsilon = 270$ kcal-mole^{-1}. As one might expect, this value is substantially smaller than the value of 500 kcal-mole^{-1} reported for a C–C bond in an n-alkane [12] or the values of 760 cal-mole^{-1} or more typical of the covalent bonds of high polymers. [10] Further, Eq. (1) indicates that T_g increases by 9.9°C for each additional carbon in the alcohol. This implies that each additional covalent bond in the alkyl backbone increases the average $\Delta\varepsilon$ by approximately 40 cal-mole^{-1}.

As the molecular weight of a primary alcohol increases, the average flex energy $\Delta\varepsilon$ can be expected to converge to a value near that of a covalent backbone C–C bond. There must be a corresponding convergence of the
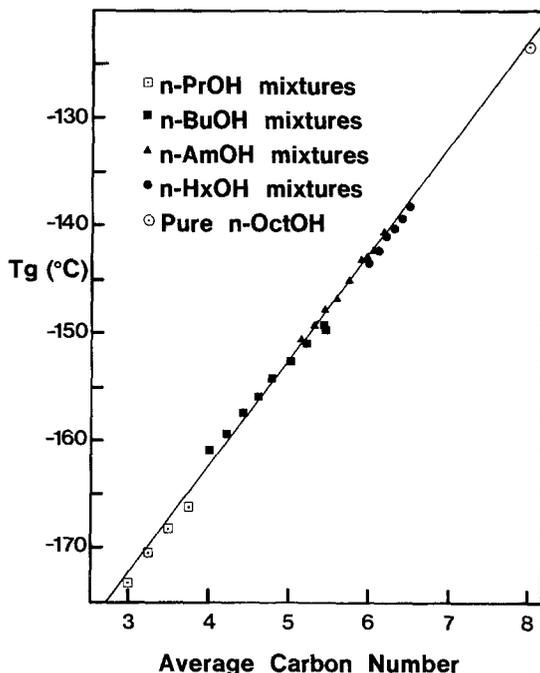
Fig. 8. Glass-transition temperature as a function of number-average length of the alkyl backbone in n-OctOH mixtures. The straight line is drawn according to Eq. (1).

T_g values. It has been suggested that the limiting T_g is that of the gamma transition in polyethylene.[8] That this hypothesis is false was disproved by its authors.[9] Our own data confirm its falsity; the n-OctOH T_g value lies very nearly at the temperature of the polyethylene gamma transition without any evidence of convergence of the alcohol T_g values. To argue that the primary alcohol T_g values should converge to this limit does not take into account the fact that a supercooled liquid of even a very high-molecular-weight primary alcohol must show a much smaller configurational entropy than in polyethylene by virtue of the constraint produced by the attachment of the alkyl backbones to the long hydrogen-bonded hydroxyl chains. It would seem more likely that the T_g values of the primary alcohols should converge to a limiting temperature near the T_g typical of the straight-chain polyolefins. In both the polyolefin and the alcohol association polymer there are alkyl side chains. If the alcohol molecule is very long, the average flex energy in the association polymer will be only slightly smaller than that in the polyolefin. Tabulated T_g values for the straight-chain polyolefins[13] then lead us to expect the primary alcohol T_g values to converge to a temperature in the vicinity of $-50°C$. If this estimate is correct, it would be necessary to
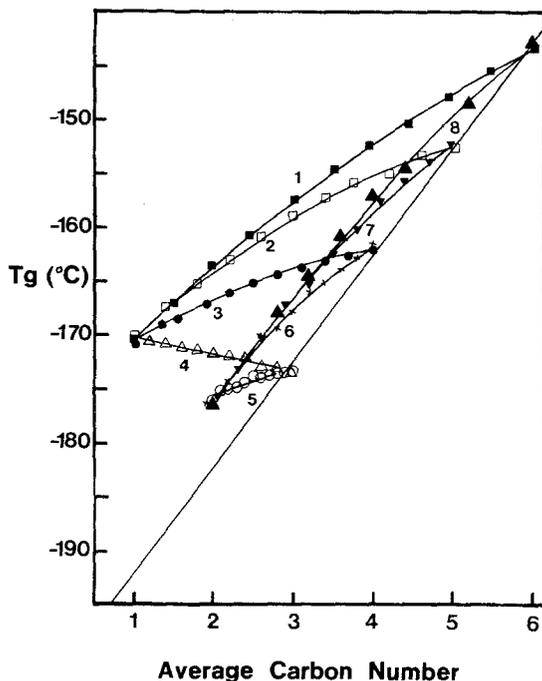
Fig. 9. Glass-transition temperature as a function of number-average length of the alkyl backbone in MeOH and EtOH mixtures. The straight line is drawn according to Eq. (1). The numbered curves apply to the following mixtures: (1) MeOH in n-HxOH; (2) MeOH in n-AmOH; (3) MeOH in n-BuOH; (4) MeOH in n-PrOH; (5) EtOH in n-PrOH; (6) EtOH in n-BuOH; (7) EtOH in n-AmOH; (8) EtOH in n-HxOH.

determine the T_g values of the primary alcohols through n-pentadecanol and beyond to secure evidence of convergence.

Our results indicate that MeOH and EtOH and their mixtures do not obey the linear congruence principle characteristic of the heavier alcohols but show higher T_g values than would be predicted on the basis of this principle. We have previously argued that this is the result of the formation of some form of crosslinkage between the hydroxyl chains at a MeOH or EtOH molecule.[4] The form of the linkage is not clear; it may result from a hydroxyl oxygen forming an additional hydrogen bond at its second acceptor site, or it may be the result of electrostatic dipole–dipole interaction between hydroxyl chains.

We can use the present data to estimate the density of crosslinkages in MeOH and EtOH. If Eq. (1) describes the T_g values of these materials in the absence of crosslinking, then the T_g values of MeOH and EtOH should be -192 and $-182°$C, respectively. The measured T_g values then indicate that crosslinkages produce a T_g increase of 22 and 6°C in MeOH and EtOH,

Table II. Comparison of T_g Values of Mixtures with the T_g Value of the Pure Alcohol Having the Same Average Backbone Length

Mixture	Average carbon number	T_g (°C)
67 mole % n-AmOH in n-OctOH	6.0	−142.8
50 mole % n-AmOH in n-HptOH	6.0	−142.6
33 mole % n-BuOH in n-HptOH	6.0	−141.0
Pure n-HxOH	6.0	−143.3
75 mole % n-BuOH in n-OctOH	5.0	−152.4
67 mole % n-BuOH in n-HptOH	5.0	−151.9
50 mole % n-PrOH in n-HptOH	5.0	−151.9
50 mole % n-BuOH in n-HxOH	5.0	−152.2
33 mole % n-PrOH in n-HxOH	5.0	−151.9
Pure n-AmOH	5.0	−152.2
75 mole % n-PrOH in n-HptOH	4.0	−162.0
67 mole % n-PrOH in n-HxOH	4.0	−162.0
50 mole % n-PrOH in n-AmOH	4.0	−161.3
Pure n-BuOH	4.0	−161.5

respectively. A theoretical expression for the T_g increment produced by cross-linking has been given by DiMarzio.[14] Equation (14a) of this author may be applied to the polymeric MeOH and EtOH associates by taking a single alcohol molecule to represent a basic repeat unit with $\gamma = 2$ and $\gamma = 3$ flexible bonds per repeat unit in MeOH and EtOH, respectively. The T_g increments found above then yield a crosslink density corresponding to an average chain length of eight MeOH molecules or 16 EtOH molecules between crosslinks. Although we have compared the light alcohols with water,[4] these results indicate that network formation in the alcohols plays a very much smaller role than it does in water.

5. CONCLUSION

The results of the present study are in accord with our previous work. Our results for the primary alcohols from n-PrOH to n-OctOH are consistent with the formation of hydrogen-bonded association chains of very great length in the supercooled liquid, while the lightest alcohols show evidence of network formation with one crosslinkage occurring for every 10 to 20 associated molecules. These results are indicative of the usefulness of glass studies as a method of probing molecular interactions.

ACKNOWLEDGMENT

REFERENCES

1. A. V. Lesikar, *Phys. Chem. Glasses* **16**, 83 (1975).
2. A. V. Lesikar, *J. Chem. Phys.* **63**, 2297 (1975).
3. A. V. Lesikar, *J. Phys. Chem.* **80**, 1005 (1976).
4. A. V. Lesikar, *J. Chem. Phys.*, to be published.
5. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Co., San Francisco, 1960).
6. A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.* **2**, 69 (1968).
7. I. Brown, *Ann. Rev. Phys. Chem.* **16**, 147 (1965).
8. J. A. Faucher and J. V. Koleske, *Phys. Chem. Glasses* **7**, 202 (1966).
9. J. V. Koleske and J. A. Faucher, *Phys. Chem. Glasses* **15**, 65 (1974).
10. J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.* **28**, 373 (1958).
11. E. A. DiMarzio and J. H. Gibbs, *J. Polymer Sci.* **40**, 121 (1959).
12. G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2* **68**, 1098 (1972).
13. M. L. Miller, *The Structure of Polymers* (Reinhold, New York, 1966), p. 288.
14. E. A. DiMarzio, *J. Res. Nat. Bur. Stand.* **68A**, 611 (1964).