

A Glass Formation Study of Binary Organic Solutions

by Yoshifumi AKAMA* and Hitoshi KANNO**

Summary

The glass transition temperatures of binary mixtures of fatty acids (formic acid to undecanoic acid in the series) with several organic solvents such as methanol, acetone etc. are measured. Glass formation is observed in most systems from the mixture of formic acid to that of hexanoic acid. In all binary systems except the fatty acid-ethyl acetate system, glass transition temperature (T_g) increase with increase in molecular weight of fatty acid in the binary solution.

1. Introduction

Interest in glassy states of various solutions has been on the rise because valuable information about structural and thermodynamic properties of the solutions can be obtained¹⁻³⁾. Recent studies by Lesiker⁴⁻⁶⁾ on binary solutions of organic compounds have revealed that glass transition temperature (T_g) can be a useful parameter representing thermodynamic properties of liquid organic compounds. It is well known that the melting temperatures of fatty acids show the up-and-down behavior across the series⁷⁾ though the up-and-downs become smaller with increase in molecular weights of fatty acids. Even number fatty acids exhibit a higher melting point than either adjacent odd number fatty acid.

Although the detailed mechanism of the up-and-down behavior is unknown, Larsson⁸⁾ explains this phenomenon in view of the structural relationships of the planes formed by the terminal methyl end groups. Therefore, it is interesting to see whether a similar up-and-down behavior may be observed in some thermodynamic properties of liquid fatty acids across the series.

Among fatty acids, only formic and acetic acids are glass-forming in pure state with a cooling rate of about 10^3 K/min. Thus, we here report the glass-formation behavior of binary mixtures of fatty acids and several organic solvents.

2. Experimental

The fatty acids used in this study were from formic acid to undecanoic acid in the series. The organic solvents used were methanol, ethanol, *n*-butyl alcohol, chloroform, ethyl acetate, *n*-amyl acetate, acetone and methyl iso-butyl ketone.

* 理工学部化学科助教授 分析化学

** 理工学部化学科教授 溶液化学, 分析化学

All chemicals were of analytical grade except methanol, ethanol, acetic acid, acetone and chloroform, which were of guaranteed grade, and were used as received.

The binary solutions were prepared by weight. Glass transition temperature were determined by a simple DTA system⁹.

The sample solution of about 0.02 ml contained in a 2 mm diameter pyrex glass cell, in which an alumel-cromel thermocouple had been inserted, was vitrified in liquid nitrogen. The cooling rate was about 10^3 K/min. Glass formation was visually checked.

The DTA measurements were carried out at a heating rate of about 5 K/min in the glass transition temperature region. Benzene was used as a reference material in the T_g measurements.

3. Results and Discussion

The typical DTA traces are shown in Fig. 1. Glass transition is characterized by a heat absorbing inflection in a DTA trace and T_g is determined in this study as an initiation point of the inflection curve.

The T_g results for the fatty acid-alcohol mixtures are shown in Fig. 2. The glass formation was observed from formic acid (methanoic acid) to *n*-caproic (hexanoic) acid for the acid—methyl alcohol and acid—ethyl alcohol systems and to *n*-heptanoic acid for the acid—*n*-butyl alcohol system.

In contrast with the zig-zag variation of melting points for fatty acids, glass transition temperatures for the acid—alcohol mixtures increase rather smoothly with increase of the molecular weight of fatty acid. Beyond heptanoic acid, no glass

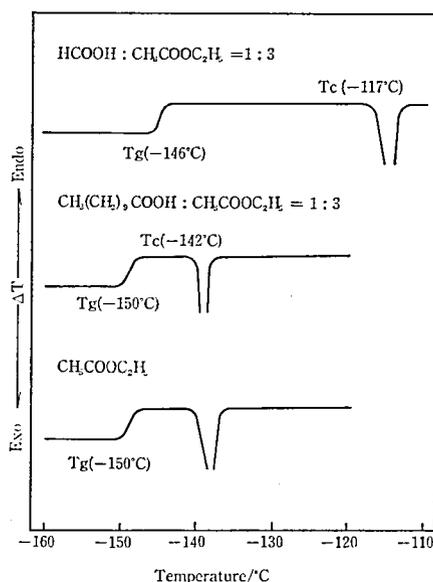


Fig. 1. Typical DTA traces for glassy organic solutions and glassy ethyl acetate.

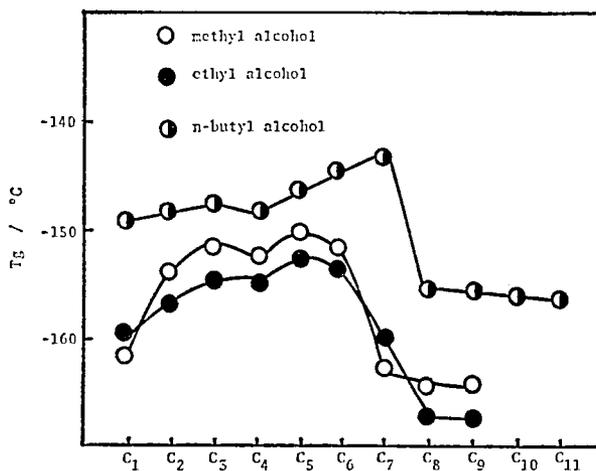


Fig. 2. Variation of T_g for binary fatty acid—alcohol mixtures. The molar ratio of alcohol to fatty acid in the mixture is 3 : 1. C_n represents a fatty acid having n carbons in a molecule, e.g., C_1 : formic (methanoic) acid, C_2 : acetic (ethanoic) acid.

formation was observed. Despite of the crystallization, which was usually accompanied with the loss of transparency, we could observe a small glass transition for the quenched acid—alcohol mixture. As the glass transition temperature is almost the same as that of the pure alcohol, we consider that the observed glass transition is due to the almost pure alcohol which remained uncrystallized in the quenching process and became a glassy state.

In a fatty acid—alcohol mixture, ester formation is expected to proceed to some extent before the T_g measurement is carried out. The T_g variations of the $\text{HCOOH—CH}_3\text{OH}$ and $\text{CH}_3\text{COOH—CH}_3\text{OH}$ mixtures are shown in Fig. 3 as a function of the standing time of the mixture. A significant fall of T_g was observed for the $\text{HCOOH—CH}_3\text{OH}$ mixture, indicating that ester formation took place to considerable degree in the mixture. On the other hand, T_g varied little with standing time for the $\text{CH}_3\text{COOH—CH}_3\text{OH}$ mixture. Therefore, it is safely concluded that there is little ester formation in the $\text{CH}_3\text{COOH—CH}_3\text{OH}$ system within a few hours' standing.

As the acid strength decreases progressively with increase in C -number of a fatty acid, ester formation should be negligible in most acid—alcohol mixtures other than the formic acid-methanol mixture. As most T_g measurements were begun within 15 minutes after the preparation of each solution, the T_g results shown in Fig. 2 are free of the effects of ester formation.

Some comment should be placed for the small dip of T_g at C_4 in the T_g curves of the fatty acid—alcohol mixtures.

As there is no similar kink in the T_g curves for other mixtures, it is considered that the dip must be related with some specific properties of the butanoic acid-alcohol

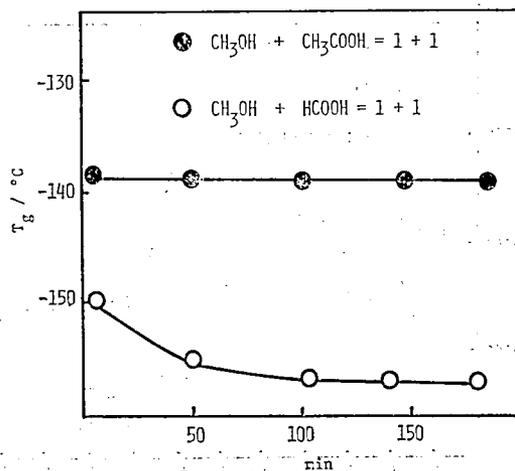


Fig. 3. Variation of T_g of the $\text{HCOOH}-\text{CH}_3\text{OH}$ or $\text{CH}_3\text{COOH}-\text{CH}_3\text{OH}$ (1 : 1) mixture as a function of standing time after the preparation of the mixture.

mixtures. However, no plausible explanation can be put forward at the moment.

The T_g results for the fatty acid—acetone or methyl iso-butyl ketone or chloroform mixtures are shown in Fig. 4. In the fatty acid mixtures with acetone or methyl iso-butyl ketone, T_g increases almost linearly with increase in C -number of fatty acid. Glass formation terminates at C_5 , beyond which no DTA measurement was done. Linear variation of T_g with C -number clearly demonstrates that thermo-

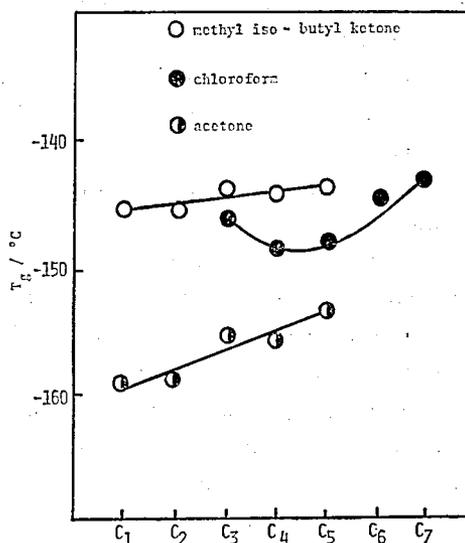


Fig. 4. Glass transition temperatures for binary fatty acid mixtures with chloroform, methyl iso-butyl ketone and acetone. The molar ratio of solvent to fatty acid in the mixture is 3 : 1.

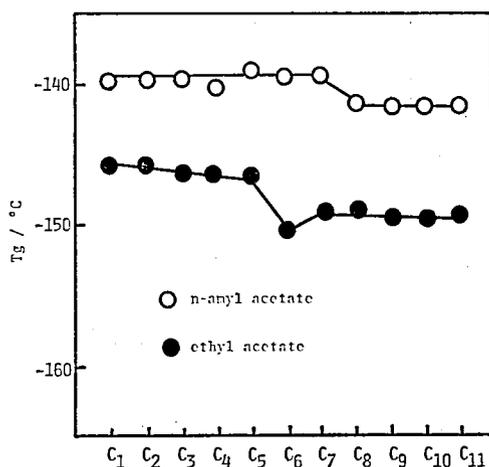


Fig. 5. Glass transition temperatures for binary fatty acid mixtures with ethyl acetate and *n*-amyl acetate. The molar ratio of ester to fatty acid in the mixture is 3 : 1.

dynamic properties such as viscosity change regularly with increase in *C*-number in these solutions. In the fatty acid—chloroform mixtures, glass formation was observed from propionic acid to heptanoic acid.

As chloroform is almost a spherical simple molecule, the mixtures of the CHCl_3 - HCOOH and CHCl_3 - CH_3COOH systems may be too simple in structure to be glass-forming at a cooling rate of about 10^3 K/min.

In acid mixtures with ethyl acetate or *n*-amyl acetate (Fig. 5), glass formation took place from formic acid to pentanoic acid for the fatty acid-ethyl acetate system and to heptanoic acid for the fatty acid—*n*-amyl acetate system. The smooth variation of T_g with acid molecular weight may be ascribed to the fact that acid molecules exist in dimeric state in these ester solvents.

It is well established that there is a close relation between viscosity and glass transition temperature of a liquid¹⁰⁾. The VTF equation, which was originally proposed to describe the viscosities of highly viscous organic liquids¹¹⁾, is known to represent the temperature dependence of viscosity for a glass-forming liquid,

$$\rho = \rho_0 \exp\left(-\frac{E}{T - T_0}\right) \quad (1)$$

where ρ_0 , T_0 and E are constants and T_0 is considered to be near T_g of the liquid. Therefore, the decrease, though small, of T_g with increase in *C*-number of the acid in the fatty acid—ethyl acetate mixtures is of particular interest because from eq. (1) it is deduced that the viscosity of the mixture decreases with increase in *C*-number of acid, at least, just above the glass transition temperature. This behavior is reverse to the normal trend that the viscosity of an organic liquid increases with increase in molecular weight in the same series of organic liquids. More T_g

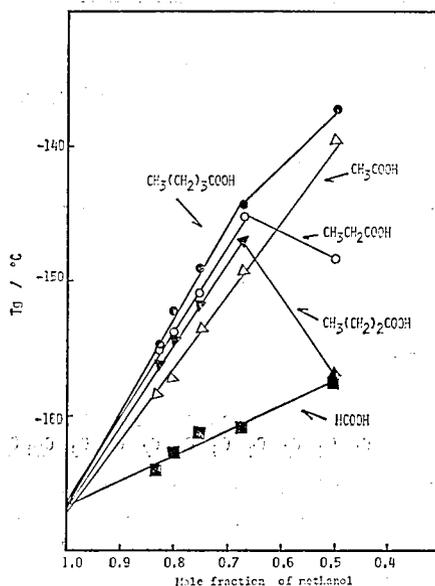


Fig. 6. Glass transition temperatures of mixtures of fatty acids with methanol as a function of the mole fraction of methanol.

measurements for various solution compositions are needed before we can obtain a full account of the anomalous behavior.

The results of extrapolation of the mixture transition temperatures to 100% of the methanol are shown in Fig. 6. Though the T_g vs composition relation is not necessarily linear, estimation of T_g for a non-glass-forming liquid has been successfully applied^{5,6}. As seen in Fig. 6, all the binary methanol solutions studied in this work give a T_g of pure methanol to be $-166 \pm 2^\circ\text{C}$, about 4°C higher than the reported value (-170°C) for pure methanol⁴. This difference is mainly due to the non-ideal behavior of the fatty acid-methanol mixture.

In the 1 : 1 mixtures with propanoic and butanoic acids, large deviation from the straight line is observed and it is concluded that the main cause for the large deviation should be due to incomplete vitrification of the mixture.

References

- 1) C. A. Angell and E. J. Sare, *J. Chem. Phys.* **52**, 1058 (1970).
- 2) H. Kanno and Y. Akama, *Chem. Phys. Lett.* **72**, 181 (1980).
- 3) H. Kanno and J. Hiraishi, *J. Phys. Chem.* **87**, 3664 (1983).
- 4) A. V. Lesikar, *J. Chem. Phys.* **63**, 2297 (1975).
- 5) A. V. Lesikar, *J. Phys. Chem.*, **80**, 1005 (1976).
- 6) A. V. Lesikar, *J. Chem. Phys.* **68**, 3323 (1978).
- 7) R. L. Eissler and J. W. Hagemann, in "Fatty Acids", edited by E. H. Pryde, Interscience, New York (1978) Chapt 9.

- 8) K. Larsson, *J. Am. Oil. Chem. Soc.* **43**, 559 (1966).
- 9) H. Kanno, I. Shirotani and S. Minomura, *Bull. Chem. Soc. Jpn.*, **53**, 2079 (1980).
- 10) G. Adam and J.H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
- 11) a) H. Vogel, *Physik Z.* **22**, 645 (1921).
b) G. Tammann and G. Hesse, *Z. Anorg. Allgem. Chem.* **156**, 245 (1926).
c) M.L. Williams, R.F. Landel and J.D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).