# DIFFERENTIAL SCANNING CALORIMETRY (DSC) STUDIES ON THE FREEZING PROCESSES OF WATER-ETHANOL MIXTURES AND DISTILLED SPIRITS

KUNIMASA KOGA and HAJIME YOSHIZUMI

─────────ABSTRACT─────────

DSC measurements of the freezing of water-ethanol mixtures in various ethanol concentrations were made in a temperature range from +20°C to −160°C. One exotherm was observed in the freezing process of each mixture. The freezing point, heat associated with the freezing process and kinetic constant of freezing ($k_f$) were determined over the entire range of the ethanol concentration from the DSC thermogram. Log $k_f$ was plotted as a function of the reciprocal of the absolute temperature ($T^{-1}$) of the mixtures. The freezing process of the mixtures in an ethanol concentration of 0~75 (V/V)% obeyed first order kinetics but at a concentration above 75%, the freezing process did not do so. The slope of log $k_f$ versus 1/T plots (d log $k_f$/d$T^{-1}$) of the mixture at the concentration below 75% was determined. The concentration below 75% was divided into four ranges (0~18.5%, 18.5~40%, 40~60%, 60~75%) from a variation in the slope of the linear plots. The results of the DSC measurements of freshly distilled spirits (raw whiskey from barley malt and grain spirits) coincided with those of simple water-ethanol mixtures. It is considered that the freezing reaction of distilled spirits proceeded by the same mechanism as that of the simple mixture of the corresponding ethanol concentration. Structures of distilled spirits as a function of ethanol concentration were discussed in terms of the interaction of water and ethanol molecules.

## INTRODUCTION

THE PROPERTIES of water-ethanol mixtures are of interest in many fields of inquiry. Franks and Ives (1966) reviewed the physico-chemical properties of the mixture from a thermodynamic point of view. Recently, the structures of water-ethanol mixtures as a function of ethanol concentration have been extensively studied with IR (Taniewska-Osinska and Grochowski, 1970), NMR(Coccia et al., 1975) and light scattering measurements (Kono et al., 1975).

Nakamura (1952) indicated that a matured water-ethanol mixture is associated each other and an unmatured non-associated, with light scattering measurements. Akahoshi (1963) showed by a dielectric method that a strong association between water and ethanol occurred in aged spirits, and suggested that these phenomena are responsible for the maturity of aged whiskey. Measuring the melting process of a frozen water-ethanol mixture with a low temperature DSC, Koga and Yoshizumi (1977) showed that structural alterations of the mixture take place at 40% and 60% ethanol concentrations, and that the strong interaction between water and ethanol in aged whiskey is not destroyed by dilution with water or mixing ethanol.

In the present manuscript, to make the structural alterations of the mixtures clearer primarily from a whiskey-making point of view, the freezing processes of water-ethanol mixtures and distilled spirits are studied with DSC measurements.

Authors Koga and Yoshizumi are with the Central Research Institute, Suntory, Ltd., Shimamoto-cho, Mishima-gun, Osaka 618, Japan.
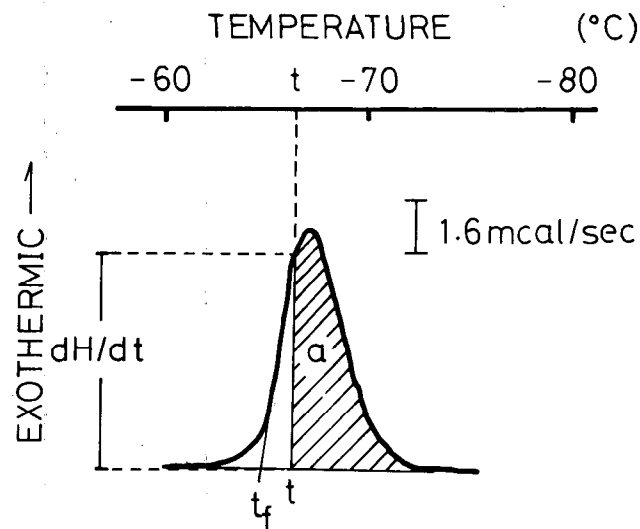
Fig. 1—DSC thermogram representative of freezing of water-ethanol mixtures at 60% ethanol concentration.

## EXPERIMENTAL

Ethanol [99.5 (V/V)%, analytical grade] was purchased from Wako Pure Chemical, Co., Kyoto, and was further purified by a fractional rectifying column (120 cm × 2 cm) packed with stainless-steel beads. The ethanol concentration of the distillate was 99.5 (V/V)%. Throughout the measurements, deionized-redistilled water was used. Freshly distilled spirits from barley malt and maize were used for DSC measurements.

The water-ethanol mixture was prepared by weight with 1-mg precision, and the ethanol concentration of a sample mixture is expressed in terms of percentage by volume (V/V%) throughout this paper.

DSC measurements of the freezing of the mixtures and distilled spirits were made with a standard type DSC-meter (Rigaku Denki Co., Tokyo). The mixture was cooled in 10°/min within a scanning temperature range of +20°C through −160°C. The detailed methods of the DSC measurements are described in a preceding paper (Koga and Yoshizumi, 1977).

For analysis of the freezing process of water-ethanol mixtures, freezing point ($t_f$), heat of freezing ($\Delta H_f$) and kinetic constant of freezing ($k_f$) were determined from DSC thermogram. Figure 1 shows a DSC thermogram representative of the freezing of water-ethanol mixture at 60% ethanol concentration. The temperature of the initial deflection of the exotherm on the thermogram was taken as a "peak temperature." The heat of freezing was estimated by integrating the peak area between the thermogram and a base-line under the peak, and expressed in terms of joules per unit weight of a sample (J/g). The kinetic constant for the freezing was calculated at various temperatures of the DSC thermogram according to the method of Donovan and Ross (1973). Deflection from the base line of the DSC curve is proportional to the rate of heat flow out of the sample (dH/dt) and this is a measure of the freezing rate. The relative amount of the unfrozen water-ethanol mixture, a, present at a temperature of t°C could be determined by measuring the fractional area under the peak below that temperature. When the freezing process of the mixture obeys first order kinetics, the kinetic constant for freezing at t°C is given by
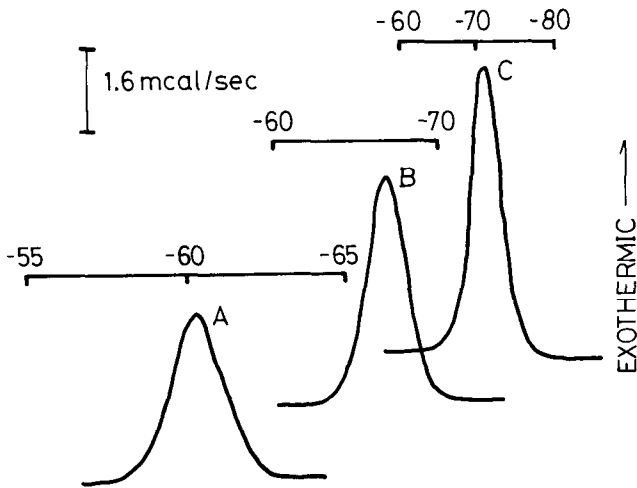
Fig. 2—Effect of the cooling rate of a calorimeter on the DSC thermogram of freezing. Ethanol concentration: 60%; Cooling rate of a calorimeter; A, 5° /min; B, 10° /min; C, 20° /min.



Fig. 3—Log $k_f$ versus 1/T plots for the freezing process of 60% water-ethanol mixtures. Cooling rate of a calorimeter: ●, 5° /min; o, 10° /min; ◑, 20° /min.

$$k_f(sec^{-1}) = \frac{v_f}{[amount \ of \ unfrozen \ mixture]} = C \cdot \frac{dH/dt}{a} \quad (1)$$

where C is a constant, and $v_f$ the freezing velocity.

The peak temperature of the thermogram was reproducible within 1°C and the heat of freezing was within 5%. All measurements were repeated at least three times to confirm the reproducibility of the thermograms.

## RESULTS

FIGURE 2 illustrates the DSC thermograms of the freezing process of a 60% water-ethanol mixture at cooling rates of 5°, 10° and 20°/min. The temperature of the exotherm, ascribable to the freezing of the mixture, depended upon the cooling rate of the calorimeter. Accordingly, the freezing point was determined by extrapolation to the rate of 0°/min. The heat of freezing did not depend on the cooling rate of the calorimeter, and was obtained as −45.0 kJ/g. On the assumption that the freezing process obeyed first order kinetics, kinetic constant was determined according to Eq (1). In Figure 3, log $k_f$ is plotted as a function of $T^{-1}$ at each cooling rate. As the plots were linear at each cooling rate, it is conceivable that the freezing process of the mixture at 60% thus obeyed first order kinetics. In the case of the chemical reaction in which the rate increases with temperature, the activation energy (E≠) of the reaction could be obtained from the slope of log $k_f$ versus $T^{-1}$ plots (d log $k_f$/d $T^{-1}$) according to the Arrhenius equation,

$$\ln k_f = \ln C - \frac{E\neq}{RT} \quad (2)$$

where C is a constant, R the perfect gas constant (1.987 cal mol$^{-1}$ K$^{-1}$), and T the absolute temperature. However, in the case of the freezing reaction, the reaction rate increases as the temperature decreases and so, the value of (d log $k_f$/d $T^{-1}$) is positive. Figure 3 shows that each value of this function does not depend upon the cooling rate, but is constant. Thus this function gives some information on the characteristics of the freezing process of the water-ethanol mixture, itself.

Exothermic heat associated with the freezing process is expressed as a function of the ethanol concentration (10~93%) as shown in Figure 4. The heat of freezing decreases with an increase in the ethanol concentration. The kinetic constant of the freezing was determined from the
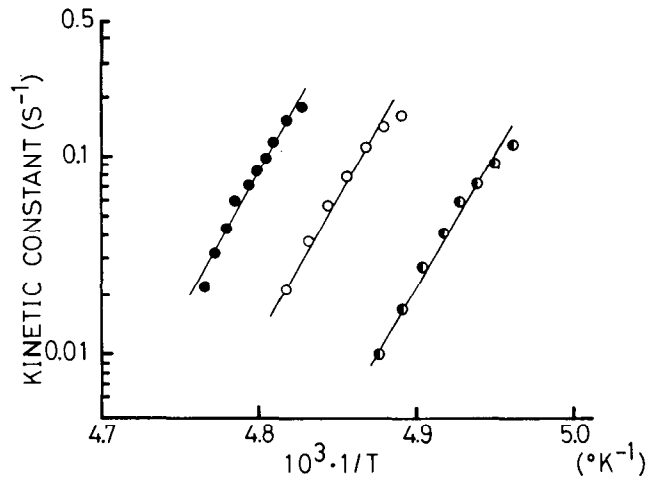
DSC thermogram of the mixtures for the entire range of ethanol concentration. The freezing process of the mixture for only ethanol concentration less than 75% obeyed first order kinetics. The value of (d log $k_f$/d $T^{-1}$) of the mixtures below 75% was obtained in the same manner as the activation energy of the Arrhenius plots and is shown as a function of the ethanol concentration in Figure 5. Within an ethanol concentration range from 0~18.5%, the value of −(d log $k_f$/d $T^{-1}$) decreases with an increase in the ethanol concentration. The values for the concentration ranges from 18.5~40% and 40~60% are constant, respectively. In the ethanol concentration range 60~75%, the value decreases with ethanol concentration. The entire ethanol concentration is divided into five ranges [(A)~(E) ranges] from a variation in the value of the function, d log $k_f$/d $T^{-1}$.

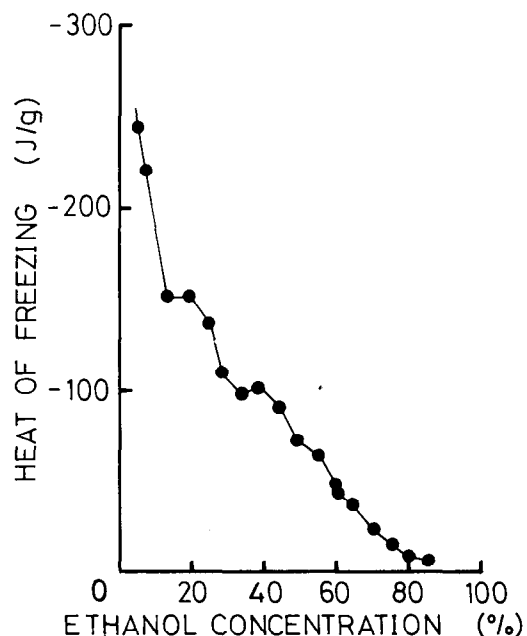After adjusting raw whiskey from barley malt and grain



Fig. 4—Relationship between the heat of freezing and ethanol concentration of water-ethanol mixtures.

Table 1—A comparison of freezing points and heats of freezing of freshly distilled spirits (raw whiskey from barley malt and grain spirits) with those of a mixture at a 60% ethanol concentration

|  | Freezing point (°C) | Heat of freezing (kJoules/g) |
| --- | --- | --- |
| Barley malt whiskey | −40.4 | −45.4 |
| Grain spirits | −40.1 | −45.7 |
| Water-ethanol mixture | −39.6 | −45.0 |

spirits to a 60% ethanol concentration with ethanol, DSC measurements of the freezing of these spirits were made. Freezing parameters ($t_f$, $\Delta H_f$ and $k_f$) of distilled spirits at 60% are practically identical with those of a 60% water-ethanol mixture as shown in Table 1 and Figure 6. After adjusting the distilled spirits to 20% and 40% with water, these samples were also subjected to DSC measurements. The freezing parameters for each sample were found to coincide with those of simple mixtures at corresponding ethanol concentrations, respectively. The freezing process of distilled spirits proceeded by the same mechanism as for the water-ethanol mixture of the corresponding ethanol concentration.

## DISCUSSION

IT IS KNOWN that the viscosity of a water-ethanol mixture has a maximum and the enthalpy of mixing of ethanol and water has a minimum at 40% at 25°C (Akahoshi, 1963; Franks and Ives, 1966; Boyne and Williamson, 1967). A contraction in volume of mixing ethanol and water has a maximum at about 60% at 25°C (Kuppers and Carriker, 1971). These phenomena are considered to closely relate with the structures of water-ethanol mixtures.

In a whiskey making process, after aging in white oak barrels at a concentration of about 60%, the matured whiskey is usually diluted to about 40% at bottling. We tried to investigate the structural alterations of distilled spirits as a function of ethanol concentration by measuring the freezing process of water-ethanol mixtures at various ethanol concentrations. The entire range of the ethanol concentration is divided into five ranges (A range: 0~18.5%; B range:
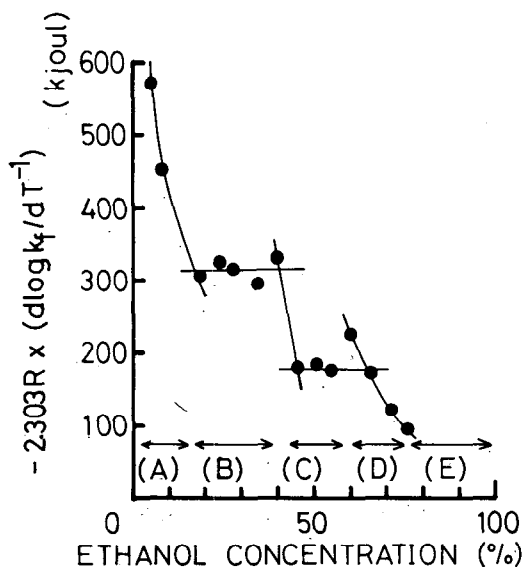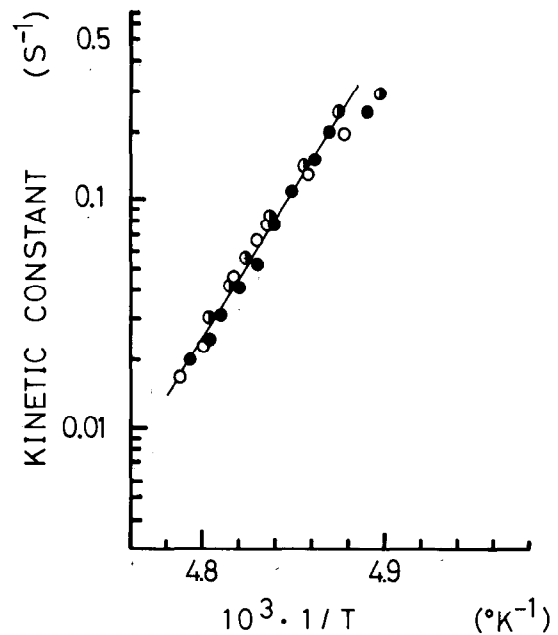
Fig. 6—Log $k_f$ versus $1/T$ plots for the freezing processes of freshly distilled spirits from barley malt ○ and maize ◑, and water-ethanol mixture ● at a concentration of 60%.

18.5~40%; C range: 40~60%; D range: 60~75%; and E range: 75~100%) from the variation in the value of (d log $k_f$/d $T^{-1}$). Considering that this function, d log $k_f$/d $T^{-1}$, can be used to evaluate the freezing process of water-ethanol mixtures in like manner of studies on protein denaturation (Multon and Guilbot, 1974), the freezing processes of the mixtures in B and C ranges proceed at a constant course, and the freezing processes in A and D ranges vary with the ethanol concentration.

A preceding paper (Koga and Yoshizumi, 1977) described some of the results on DSC measurements of the melting processes of frozen water-ethanol mixtures. These measurements indicate that structural alterations in the mixtures occur at 40% and 60%. Especially, the temperature of the endotherm, ascribable to the melting of ethanol, shifts from −74°C to −62°C at about 40% ethanol concentration. The result may show that ethanol molecules of the mixtures at an ethanol concentration above 40% are in more intimate interaction with water than those at a concentration below 40%. By NMR measurements of the mixtures, Coccia et al. (1975) studied the changes of ethanol and water OH chemical shifts of water-ethanol mixtures over the entire concentration range. From this experiment, the entire range of the ethanol concentration is divided into five ranges and each range almost agreed with that obtained from DSC measurements. Coccia et al. (1975) also have proposed that water-ethanol mixture at a concentration below about 40% keeps the structure of water, and at a concentration above about 40%, the water structure is progressively disrupted by an increase in the ethanol concentration. This mechanism of molecular association in the mixtures supports our interpretation of the shift in the melting point of ethanol in water-ethanol mixtures at about 40%. Usually, distilled spirits are bottled at about 40% ethanol concentration. This may be related to the structures of eater-ethanol mixtures which keep the water structures in a concentration range from 0~40%.

The relationship between the freezing point and ethanol concentration of the mixture is shown in Fig. 7. This result coincides with that already published (Seidell, 1941). The freezing points of mixtures at concentration above 93% are
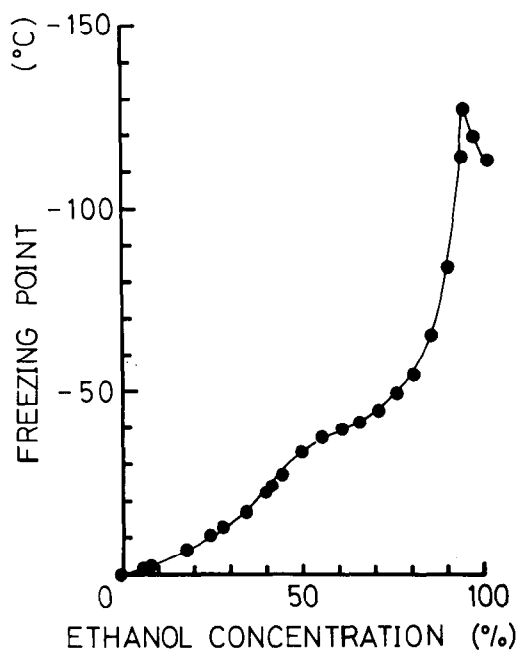
Fig. 5—Relationship between the value of (d log $k_f$/d $T^{-1}$) and ethanol concentration of water-ethanol mixtures.

*Fig. 7—Relationship between the freezing point and ethanol concentration of water-ethanol mixtures.*

lower than that of pure ethanol (−114°C). The vapor pressures of mixtures for the corresponding range of ethanol concentrations are also well known to be higher than that of pure ethanol, e.g. the 95% azeotrope. This may show that the addition of a small quantity of water to ethanol promotes the hydrophobicity of ethanol molecules.

On the other hand, conventionally, whiskey is stored in a white oak barrel at a concentration of 60%. The structure of a water-ethanol mixture at a concentration of 60% has not been understood concretely. However, the present result suggests that structural alterations of the mixture take place at a 60% ethanol concentration (Fig. 5). The preceding paper (Koga and Yoshizumi, 1977) also suggested that the portion of strongly interacted water-ethanol is least at 60% ethanol concentration. In other words, the activity of ethanol in water-ethanol mixtures is maximal at 60%. It is known that the maximum amount of acid materials and

phenolic compounds are extracted from the barrel by a water-ethanol mixture of about 60% (Liebmann and Rosenblatt, 1943). When whiskey is stored at 60% ethanol concentration, it may result in an increase in the interaction between ethanol and the white oak barrel, and effectively make the whiskey mature.

In the preceding paper (Koga and Yoshizumi, 1977), the melting process indicated three endotherms, whereas, in this paper, we found that the freezing process has only one exotherm. It is considered that the freezing reaction proceeds by a vitreous transition. Additional studies are in progress to investigate the differences in the melting and freezing DSC curves.

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