

## Temperature corresponding to ultrasonic velocity maximum studies in aqueous solutions

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**Abstract.** Ultrasonic velocities in aqueous solutions of acetamide, dimethyl urea and  $\beta$ -alanine at different concentrations in the temperature range of about 60°C to 80°C have been measured using an interferometer technique with an accuracy of  $\pm 0.003\%$ . The temperature corresponding to velocity maximum at different concentrations is evaluated with an accuracy of  $\pm 0.2^\circ\text{C}$ . The results are discussed in the light of the structure-breaking property of these substances in water.

**Keywords.** Ultrasonic velocities; aqueous solutions; acetamide; dimethyl urea;  $\beta$ -alanine.

### 1. Introduction

Water is a unique liquid having a velocity maximum at 74°C. All pure liquids except water (Pancholy 1953) and heavy water (Randall 1932) exhibit negative temperature coefficient of sound velocity. Several workers (Frank and Wen 1957; Nemethy and Scheraga 1962; Hall 1948 and Davis and Litovitz 1965) have tried to explain the anomalous behaviour of water. According to the two-state model, liquid water can be regarded as an equilibrium mixture of essentially two species, namely close-packed and open-packed structures. Increase in temperature produces volume expansion of both the species resulting in a negative temperature coefficient of sound velocity (Eyring and Kinoid 1937, 1938). In addition, there will be an equilibrium shift between the two species due to the rupture of the hydrogen bonds with an increase in temperature. As the temperature is raised the concentration of close-packed structures increases leading to a positive temperature coefficient of sound velocity. The sound velocity maximum at 74°C can be visualised as a consequence of these two opposing tendencies. Any process that changes the structural equilibrium in water influences the temperature corresponding to sound velocity maximum (TVM). A shift in TVM towards lower temperatures can be assumed to be due to the rupture of open-packed structures in water and vice versa.

The addition of a solute to water either breaks or builds the structure of water and hence results in shift of TVM of water. Besides the structural effect, the dilution effect also contributes to the shift in TVM. Such studies have been made by a number of workers, namely Mikhailov and his coworkers (Mikhailov and Shutilov 1956; Mikhailov *et al* 1957; Mikhailov and Syrinkov 1960; Mikhailov 1962); Marks (1959, 1960); Pancholy and Singal (1960); Gnanamba and Ramachandra Rao (1969); Nomoto and

Endo (1970, 1971, 1973); Subrahmanyam and Raghavan (1973); Sivakumar (1976); Sivakumar *et al* (1973) and Prabhakara Rao and Reddy (1976). The effect of liquid solutes on the structure of water has been studied by Willard (1947) and Subrahmanyam and Manohara Murthy (1974, 1975). In the present investigation we have studied the aqueous solutions of acetamide, dimethyl urea and  $\beta$ -alanine.

## 2. Experimental

Ultrasonic velocity in aqueous solutions has been determined using a single crystal interferometer technique with an accuracy of  $\pm 0.003\%$ . The experimental set-up has been described previously by Sivakumar *et al* (1973). For solutions studied in the present work, the shape of the velocity versus temperature curve is similar to that of pure water. Hence a transparent template of the curve for water was used to fix the value of TVM with an accuracy of  $\pm 0.2^\circ\text{C}$ .

## 3. Results and discussion

The variation of ultrasonic velocity with temperature in aqueous solutions of acetamide, dimethyl urea and  $\beta$ -alanine has been presented in figures 1 to 3. The shift in TVM i.e.  $\Delta\text{TVM}$  as a function of concentration for all the solutions studied in this investigation together with the data of urea (Prabhakara Rao and Reddy 1976) is

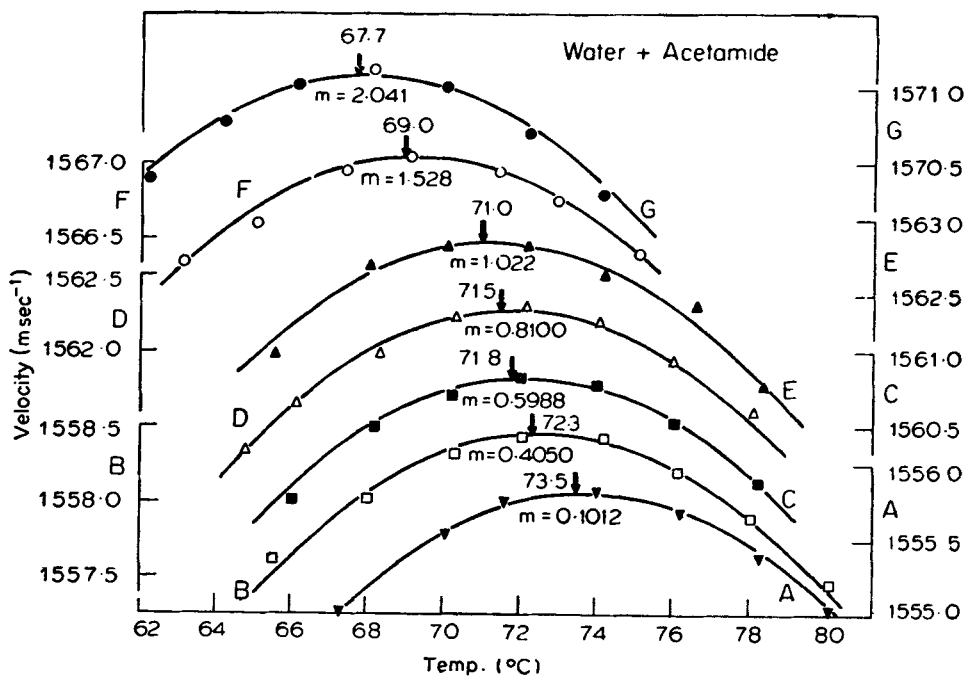


Figure 1.

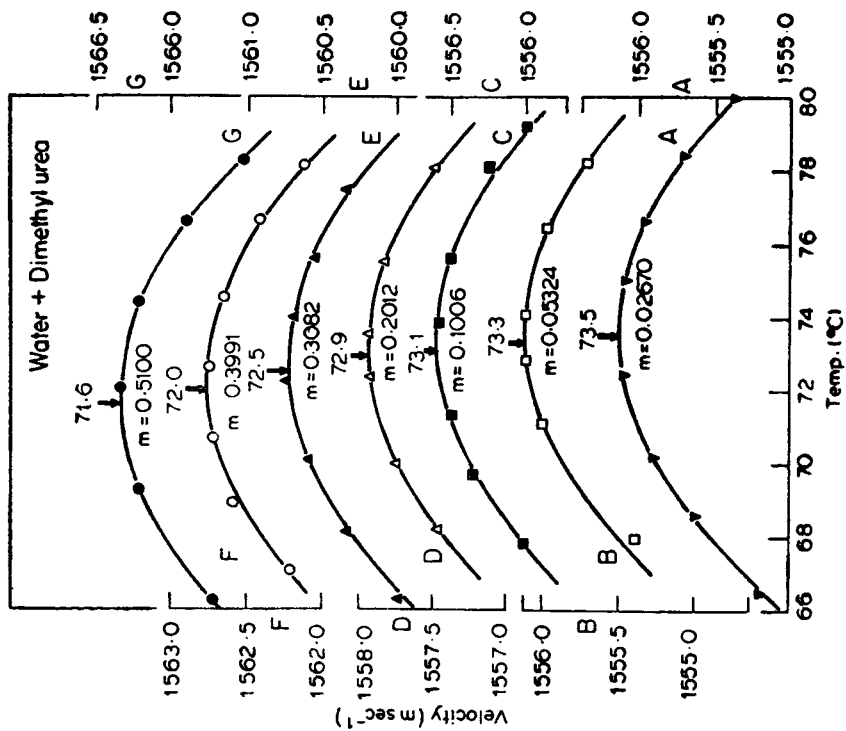


Figure 2.

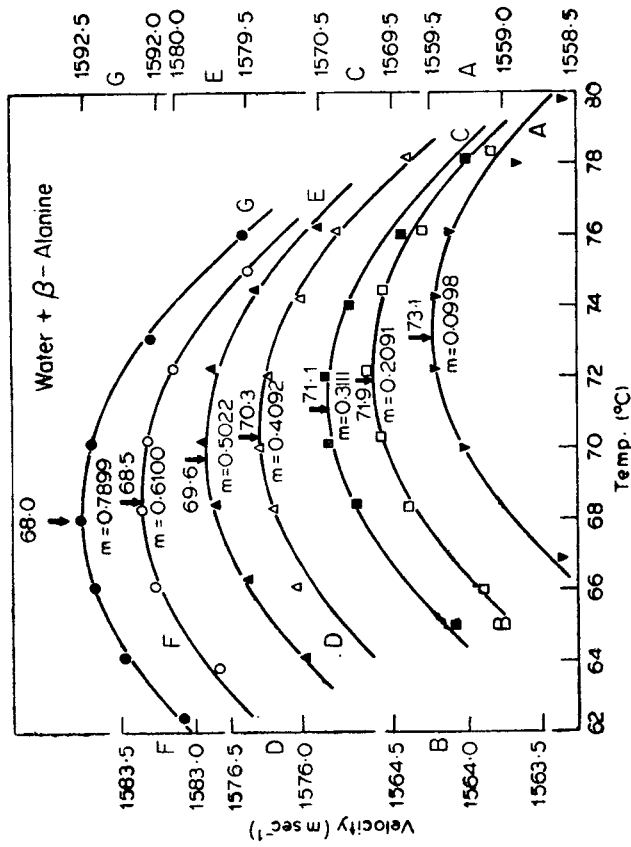


Figure 3.

Figures 1-3. Variation of ultrasonic velocity with temperature in aqueous solutions. 1. acetamide 2. dimethyl urea 3. β-alanine

shown in figure 4. It was found that in solutions of all the substances, the shift in TVM is negative, which indicates that the addition of these substances in water causes break-up of the open-packed clusters in water.

The behaviour of acetamide, a structure breaker of water, is in accordance with that obtained from absorption studies by Hammes and Swann (1967). Because of the decreased classical absorption of the aqueous solutions of acetamide to that of water, they have assumed that the effect of adding acetamide is to break the structure of water. The TVM and absorption studies provide a qualitative estimate of the effect caused on the structure of water. However when compared with the structure-breaking effect caused by urea, Hammes and Swann (1967) stated that acetamide is half effective as urea in breaking the structure of water. This is because the presence of  $\text{CH}_3$  group in acetamide favours hydrogen bonding between the two molecules. From the variation of velocity with temperature Nomoto and Endo (1970) also indicated that acetamide is a structure-breaker. From figure 4 it is seen that acetamide is more than half effective as that of urea in breaking the clusters of water.

In the case of dimethyl urea the TVM shifts towards lower temperature, indicating that the effect of dissolving dimethyl urea causes the open-packed clusters to break up in water. Arakawa *et al* (1970) studied the ultrasonic absorption in aqueous solutions and found that at  $20^\circ\text{C}$  the  $(a/f^2)_{\text{structural}}$  decreases and then increases slightly with the increase of dimethyl urea in solution. The decrease in the value of  $(a/f^2)_{\text{structural}}$  is attributed to the structure-breaking effect. In the present investigation dimethyl urea shows structure-breaking effect throughout the range of concentrations studied. It may also be pointed out that in the present range of study, the shift in TVM varies linearly with concentration (figure 4). In this substance there are two methyl groups which prefer more structure forming effect. In spite of the general trend, the structure breaking effect is more than in urea which contradicts with the general trend.

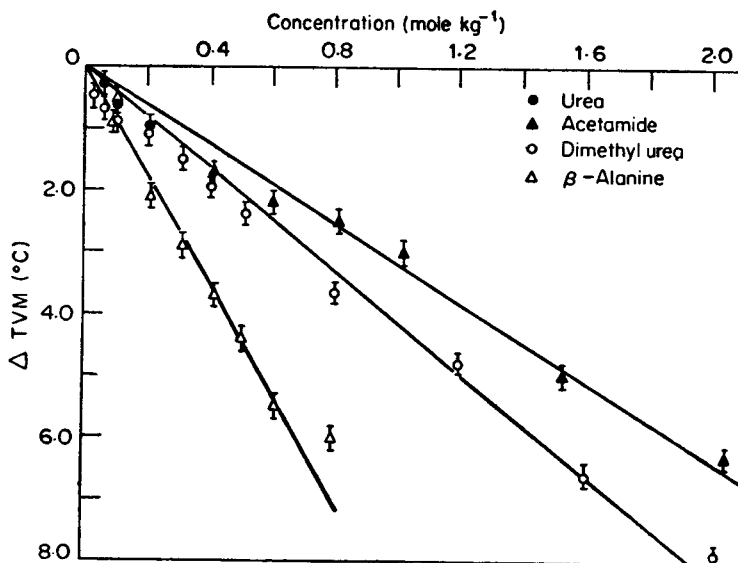


Figure 4. Shift in TVM ( $\Delta\text{TVM}$ ) as a function of concentration in urea (Prabhakara Rao and Reddy 1976), acetamide, dimethyl urea,  $\beta$ -alanine and D-glucose.

The other molecule studied in this investigation is  $\beta$ -alanine, which is an amino acid. In the solutions of  $\beta$ -alanine the TVM also shifts towards lower temperatures, which means that  $\beta$ -alanine breaks the clusters of water. Moreover in this case the shift in TVM is large when compared with other substances studied here. From the partial molal specific heat capacity data, Kresheck and Benjamin (1964) concluded that  $\beta$ -amino substitution solute has a structure-breaking influence on the solvent and glycine is a weaker structure-breaker. The heat capacity at infinite dilution for a structure-breaking solute should be less than that of the solid. In the case of  $\beta$ -alanine the apparent molal heat capacity at infinite dilution is less than that of the solute (Gucker and Allen 1942). According to Fuoss theory (Fuoss 1936) the limiting slope of the partial volume and partial molal heat capacities should be greater for  $\beta$ -alanine than for glycine but the opposite is observed by Gucker *et al* (1942). This discrepancy may be envisaged due to the increased close-packing structure of water molecules by the addition of  $\beta$ -alanine than that of glycine. The results of Gucker *et al* (1950) show that the adiabatic compressibility in the solutions of  $\beta$ -alanine decreases with increase in concentration. This rapid decrease may be attributed to the increase of close-packed structures of water. Gucker and Allen (1942) studied the molal volume of aqueous solutions of  $\beta$ -alanine. They observed a decrease of 4.7 ml in molal volume at infinite dilution of  $\beta$ -alanine for which the molal volume is 63.4 ml. They have attributed this decrease to the greater electrostriction in the liquid than that of close-packed solid  $\beta$ -alanine. This decrease in molal volume at infinite dilution also stands as evidence to the structure-breaking effect of  $\beta$ -alanine in water. Hence it may be concluded that the effect of addition of  $\beta$ -alanine is to break the clusters of water.

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