Effect of mixed electrolytes on the temperature of sound velocity maximum of water

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Effect of mixed electrolytes (KCl + KBr), (KCl + KI) and (KBr + KI) on the temperature of sound velocity maximum (TSVM) of water, \( T_w \), has been studied by determining the ultrasonic velocity with an accuracy of ± 0.003% using single crystal variable path interferometer working at 3 MHz. The velocity measurements were carried out at \( 2^\circ \)C intervals over a range of 5°C on either side of TSVM of the solution. The accuracy in fixing TSVM is ± 0.2°C. The structural contribution to the shift in \( T_w \) of pure water due to the addition of mixed electrolytes, \( \Delta T_{str} \), has been found to be negative and increasing with concentration of mixed electrolytes. At any given concentration \( \Delta T_{str} \) of (KCl + KBr) > (KCl + KI) > (KBr + KI). \( \Delta T_{str} \) is also found to vary linearly with ionic strength of the mixed electrolyte solutions, and at any given ionic strength \( \Delta T_{str} \) of (KCl + KBr) > (KCl + KI) > (KBr + KI). The results are explained in terms of enhancement in the structure breaking nature of Cl\(^-\), Br\(^-\) and I\(^-\) due to K\(^+\) and is found to be in the order of I\(^-\) > Br\(^-\) > Cl\(^-\).

**Keywords:** Electrolytes, Sound velocity, Water

**IPC code:** G 01 N

### 1 Introduction

Pure water shows extrema in many of its physical properties as a function of temperature such as maximum density at 3.98°C, minimum adiabatic compressibility at 64°C, maximum sound velocity at 74°C and maximum specific acoustic impedance at 56.4°C. This behaviour of water could be explained on the basis of two-state model of water common to many theories\(^1\)\(^-\)\(^5\).

The effect of electrolytes on the temperature of sound velocity maximum\(^6\)\(^-\)\(^16\) has been studied extensively. The structural contribution to the shift in the temperature of sound velocity maximum has been evaluated after accounting for dilution effect. Based on the sign and magnitude of the structural shift produced by different electrolytes, the respective anions and cations have been classified as structure promoters or structure disrupters. The studies carried out on alkali halides\(^13\)\(^,\)\(^14\) indicate Li\(^+\) as a strong structure promoter whereas Na\(^+\) as a very weak-structure promoter. K\(^+\), Rb\(^+\), Cl\(^-\), Br\(^-\), I\(^-\) and F\(^-\) have been classified as structure disrupters.

Literature survey indicates that only the effect of single electrolytes on the temperature of sound velocity maximum has been studied. It will be interesting to see how the structural interactions would be in the presence of a third ion. Hence, the effect of mixed electrolytes on the temperature of sound velocity maximum of water has been studied. Recently, the authors studied the effect of mixed electrolytes (NaCl + NaBr), (NaCl + NaI), (NaBr + NaI) and (NaCl + KCl), (NaBr + KBr), (NaI + KI) on temperature of sound velocity maximum of water, respectively\(^17\)\(^,\)\(^18\), and the results have been found to be useful in deliniating the structural propensities of unlike ions in the presence of the common ion of the mixed electrolytes. The present paper deals with the studies on the effect of mixed electrolytes namely (KCl + KBr), (KCl + KI) and (KBr + KI) on the temperature of sound velocity maximum of water.

### 2 Experimental Details

Ultrasound velocity was determined using a single crystal variable path interferometer working at 3 MHz. For each solution, measurements were made in the range 64-80°C at \( 2^\circ \)C intervals. A tri-tet crystal controlled oscillator with a frequency stability of ±1 Hz was used to excite the quartz transducer. The voltage variations across the transducer were observed using a difference amplifier followed by an electronic voltmeter.

The mechanical assembly of the interferometer was immersed in a thermostatic water-bath whose
temperature was controlled to ± 0.01°C. Temperature gradients inside the experimental liquid were minimized by stirring it periodically. The thermostat and the electronic assembly were housed in an air-conditioned room whose temperature was maintained at 20 ± 1°C. This resulted in improved stability of the crystal oscillator and the efficiency of the temperature control. The accuracy of wavelength measurement is ±0.0025% and the overall accuracy in the measurement of ultrasonic velocity is ±0.003%. The details regarding the mechanical assembly of the interferometer, electronic circuity used and accuracy of ±0.05 ms$^{-1}$ relalizable in ultrasonic velocity measurement are presented in our earlier paper$^{19}$.

3 Results

Ultrasonic velocities measured as a function of temperature in the range 64-80°C at 2°C intervals in aqueous solutions of (KCl + KBr), (KCl + KI) and (KBr + KI) are presented in Figs (1-3), respectively. The velocity versus temperature curves for all the solutions studied have the same shape as the curve for pure water. Hence, a transparent template of the ultrasonic velocity-temperature curve for pure water itself was used to fix TSVM of the solutions. The accuracy in fixing TSVM is 0.2°C.

4 Discussion

The shift in the temperature of sound velocity maximum of water caused by the addition of mixed electrolytes is given by

$$\Delta T_{obs} = (T_s - T_w) = (T_s - 74) \quad \cdots (1)$$

where $T_s$ and $T_w$ represent the TSVM of aqueous mixed electrolyte solution and water, respectively. This shift may be thought of as arising due to two effects namely dilution and structural effect. The dilution effect is always negative, that is towards lowering of TSVM of water. The structural effect arises as a result of interaction between the solute and the solvent and it will be positive if the hydrogen bonded structure of water is stabilized against thermal collapse by the solute and negative if the hydrogen bonded structure of water is destabilized by the presence of solute creating monomers of water molecules. To separate these two effects it is necessary to evaluate the effect of dilution on TSVM of water by the addition of the solutes. This can be done combining the expression representing the temperature dependence of sound velocity in water and in the solutes.

According to Willard$^{20}$ the temperature dependence of sound velocity in pure water conforms to the relation

$$u_1 = 1557 - 0.0245 (74 - t)^2 \quad \cdots (2)$$

where $t$ represents the temperature in °C.

If $u_2$ and $u_3$ represent the sound velocities in electrolyte 1 (solute 1) and in electrolyte 2 (solute 2) of the mixed electrolyte, then their temperature dependence may be represented as:

$$u_2 = u_2^o - \alpha_2 t \quad \cdots (3)$$

and

$$u_3 = u_3^o - \alpha_3 t \quad \cdots (4)$$

where $u_2^o$ and $u_3^o$ are the velocities of sound in the electrolyte 1 and electrolyte 2 at 0°C and $\alpha_2$ and $\alpha_3$ are temperature coefficients of sound velocities in electrolyte 1 and electrolyte 2 respectively.

Assuming additivity of internal energy, the velocity of sound in the aqueous mixed electrolyte solution can be written as$^{21}$:

$$u^2 = w_1 u_1^2 + w_2 u_2^2 + w_3 u_3^2 \quad \cdots (5)$$

where $w_1$, $w_2$ and $w_3$ represent the weight fraction of water, electrolyte 1 and electrolyte 2, respectively.

Substituting Eqs (2), (3) and (4) in Eq. (5), we get:

$$u^2 = w_1 [1557 - 0.0245 (74 - t)^2]^2 + w_2 [u_2^o - \alpha_2 t]^2 + w_3 [u_3^o - \alpha_3 t]^2 \quad \cdots (6)$$

Differentiating Eq. (6) with respect to temperature and making use of the condition that:

$$\left( \frac{du}{dt} \right)_{t = T_s} = 0$$

one can get:

$$w_1 [1557 - 0.0245 (74 - T_s)^2]^2 (0.049) (74 - T_s) - w_2 (u_2^o - \alpha_2 T_s) \alpha_2 = w_3 (u_3^o - \alpha_3 T_s) \alpha_3 = 0 \quad \cdots (7)$$
The term in the square bracket in Eq. (7) represents the velocity of sound in pure water at the temperature of sound velocity maximum in the solution, \( T_s \), and can be replaced by 1557 ms\(^{-1} \) if \( T_s \) does not differ appreciably from 74°C. Hence,

\[
w_i(1557)(0.049)(74-T_s) = w_2(u_2^o-\alpha_2 T_s)\alpha_2 + w_3(u_3^o-\alpha_3 T_s)\alpha_3 \tag{8}
\]

Simplifying, one can get:

\[
T_s = \frac{(5646w_1-\alpha_2 u_2^ow_2-\alpha_3 u_3^ow_3)}{(76.3w_1-w_2\alpha_2^2-w_3\alpha_3^2)} \tag{9}
\]

If there is no change in the structure of water due to the addition of mixed electrolyte, then, \( T_s \) given by Eq. (9) represents the ideal value of the temperature of sound velocity maximum in the solution. That is,

\[
T_s = (T_s)_{id} \tag{10}
\]

If the hydrogen bonded structure of water is modified by the presence of the mixed electrolyte, then, TSVM observed experimentally \( (T_s)_{exp} \) will differ from that of the ideal value \( (T_s)_{id} \). Hence, the structural contribution to the shift in TSVM of water due to the addition of the mixed electrolyte, is given by:

\[
\Delta T_{str} = (T_s)_{exp} - (T_s)_{id} \tag{11}
\]

The magnitude and sign of \( \Delta T_{str} \) represent the strength and nature of structural interactions between the solute (mixed electrolyte) and water.

To calculate \( (T_s)_{id} \), due to the addition of mixed electrolyte, one needs \( u_2^o, u_3^o, \alpha_2 \) and \( \alpha_3 \). These parameters can be evaluated from the data on temperature dependence of elastic constants. Since, the solutes used are solid electrolytes, we have three velocities associated with sound wave propagation namely one longitudinal and two transverse. Since there is no reason to prefer any one of these velocities we may use the mean sound velocity, \( u_m \), given by the following relation:

\[
u_m = \left[ \frac{1}{3}\left( \frac{1}{u_l^o} + \frac{2}{u_t^o} \right) \right]^{-1/3} \tag{12}
\]

where \( u_l \) and \( u_t \) represent the longitudinal and transverse sound wave velocities in the poly-crystalline aggregates of the electrolyte. To evaluate the Debye characteristic temperature of polycrystalline samples, the average velocity normally used is that given by Eq. (12). In the present work, mixed electrolyte combinations are chosen from the alkali halides KCl, KBr and KI. \( u^o \) and \( \alpha \) for KCl, KBr and KI have been evaluated making use of the data on elastic constants and their temperature dependence\(^{22-24} \). The method followed to calculate \( u_l \) and \( u_t \), from elastic constant data, necessary to evaluate \( u_m \), making use of Eq. (12), is given in an earlier paper\(^{25} \). By least square-fitting of \( u_m \) versus temperature data to Eq. (3) \( u^o \) and \( \alpha(u_2^o \text{ or } u_3^o \text{ and } \alpha_2 \text{ or } \alpha_3 \text{ as the case may be) } \) have been evaluated. The values of \( u^o \) and \( \alpha \) for KCl, KBr and KI are 2449 ms\(^{-1} \), 0.50 ms\(^{-1}\)K\(^{-1} \), 1334 ms\(^{-1} \), 0.24 ms\(^{-1}\)K\(^{-1} \); and 1538 m s\(^{-1} \), 0.44 m s\(^{-1}\)K\(^{-1} \), respectively.

The TVSM in aqueous solutions of mixed electrolytes namely (KCl + KBr), (KCl + KI) and (KBr + KI) determined using the template of the curve for pure water are presented in Table 1. The values of \( \Delta T_{obs} \) for the mixed electrolytes (KCl + KBr), (KCl + KI) and (KBr + KI) as a function of

<table>
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<th>( w )</th>
<th>( \mu )</th>
<th>( (T_s)_{exp} )</th>
<th>( (T_s)_{id} )</th>
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weight fraction of the mixed electrolytes are presented in Fig. 1. These results indicate that \( \Delta T_{\text{obs}} \) values for (KCl + KBr), (KCl + KI) and (KBr + KI) are negative. This negative shift increases linearly with increase in the weight fraction of the mixed electrolytes in the case of (KCl + KBr) and (KCl + KI) and quadratically with weight function in the case of (KBr + KI). The values of \( \Delta T_{\text{str}} \) for mixed electrolytes (KCl + KBr), (KCl + KI) and (KBr + KI) as a function of weight fraction of the mixed electrolyte are presented in Fig. 2. \( \Delta T_{\text{str}} \) for mixed electrolytes (KCl + KBr) and (KCl + KI) are negative and the negative shift increases linearly with increase in the weight fraction. \( \Delta T_{\text{str}} \) for (KBr + KI) is negative and negative shift increases non-linearly with increase in the weight fraction. This non-linear dependence indicates modification of the structural interactions of unlike ions by the like ions when mixed electrolyte is present in water. The viscosity \( B \)-coefficient\(^ {26} \) and the activation energy of viscous flow data\(^ {27} \) classify K\(^ + \), Cl\(^ - \), Br\(^ - \) and I\(^ - \) as structure breaking ions. The studies on the effect of alkali halides on the temperature of sound velocity maximum\(^ {6-16} \) of water also indicate K\(^ + \), Cl\(^ - \), Br\(^ - \) and I\(^ - \) as structure disrupting ions. The viscosity \( B \)-coefficient\(^ {27} \) for K\(^ + \), Cl\(^ - \), Br\(^ - \) and I\(^ - \) are \(-0.007, -0.007, -0.032 \text{ and } -0.080 \), respectively.

\( \Delta T_{\text{obs}} \) and \( \Delta T_{\text{str}} \) for mixed electrolytes are negative throughout the concentration range and at any given concentration are in the order (KCl + KBr) > (KCl + KI) > (KBr + KI) indicating structure breaking efficiency of K\(^ + \) > Br\(^ - \) > Cl\(^ - \). The non-linear variation for (KBr + KI) may be considered to be due to the influence of K\(^ + \) ion on the strong structure breaking ions Br\(^ - \) and I\(^ - \). To delineate further the effect of like ion K\(^ + \) on unlike ions Cl\(^ - \), Br\(^ - \) and I\(^ - \) in aqueous mixed electrolyte solution, the authors have examined the additivity rule taking the data available in literature\(^ {13,14} \) for individual electrolytes.

\[ \Delta = (\Delta T_{\text{str}})_{\text{ME}} - ((\Delta T_{\text{str}})_{\text{E1}} + (\Delta T_{\text{str}})_{\text{E2}}) \]  \quad \text{(13)}

where suffixes E1 and E2 and ME stand for electrolyte 1 and electrolyte 2 and mixed electrolyte respectively. The values of \( \Delta \) calculated, using the following relation:

As can be seen from Fig. 3, \( \Delta \) for (KCl + KI) is negative and increases with weight fraction. This indicates that in the presence of K\(^ + \) the structural propensities of Br\(^ - \) and I\(^ - \) are modified. The overall effect is an increase in the structure breaking nature of I\(^ - \). Similarly \( \Delta \) for (KBr + KI) is also negative indicating that the structure breaking nature of Br\(^ - \) and I\(^ - \) may be enhanced in the presence of K\(^ + \) (Fig. 3) at any given concentration. This trend indicates that enhancement in the structure breaking efficiency of Cl\(^ - \), Br\(^ - \) and I\(^ - \) due to K\(^ + \) is in the order of I\(^ - \) > Br\(^ - \) > Cl\(^ - \).

The structural interactions like ion-solvent, ion-ion and solvent-solvent interactions in aqueous

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**Fig. 1**—\( \Delta T_{\text{obs}} \) versus weight fraction of mixed electrolytes, (KCl + KBr), (KCl + KI) and (KBr + KI). A \( \rightarrow \) KCl + KBr; B \( \rightarrow \) KCl + KI; C \( \rightarrow \) KBr + KI.

**Fig. 2**—\( \Delta T_{\text{str}} \) versus weight fraction of mixed electrolytes, (KCl + KBr), (KCl + KI) and (KBr + KI). A \( \rightarrow \) KCl + KBr; B \( \rightarrow \) KCl + KI; C \( \rightarrow \) KBr + KI.
electrolytic solutions having common ions have been investigated applying physico-chemical techniques at constant ionic strength. In the present study, the effect of common ions on unlike ions has been investigated by varying the concentrations of mixed electrolytes, that is, by varying the ionic strength. In the case of monovalent electrolytes the ionic strength of the aqueous mixed electrolytic solutions is equal to the molarity of the common ion. Since, the present investigation is aimed at deliniating the effect of common ion on the structural propensities of unlike ions, it is essential to examine whether the conclusions drawn are consistent or not when the studies are made on solutions with increase in ionic strength instead of at constant ionic strength. The ionic strengths of the mixed electrolytic solutions studied are presented in Table 1. Since $\Delta T_{\text{str}}$ values reflect the structural interactions, $\Delta T_{\text{str}}$ versus ionic strength for the mixed electrolytes studied are presented in Fig. 4. Within the limits of experimental error, $\Delta T_{\text{str}}$ varies linearly with ionic strength for the mixed electrolytes (KCl + KBr), (KCl + KI) and (KBr + KI). This behaviour may be considered to indicate that the results and conclusions drawn, that is,
enhancement in the structure breaking efficiency of Cl\(^-\), Br\(^-\) and I\(^-\) due to the presence of K\(^+\) ions may not differ whether investigations are made at constant ionic strength or by varying ionic strength, of the mixed electrolyte solutions. However, further investigations on mixed electrolytic solutions having common ions would be undertaken at constant ionic strength also.

5 Conclusions
(1) The destabilization of the hydrogen bonded structure of water is more effective when mixed monovalent electrolytes with common ion are present, than in the presence of monovalent single electrolyte.

(2) The structural contributions to the shift in TSVM, \(\Delta T_{str}\), due to the presence of mixed electrolytes (KCl + KBr), (KCl + KI) and (KBr + KI) are found to be negative indicating the break down of the hydrogen bonded structure of water leading to the formation of monomers and at any given concentration \(\Delta T_{str}\) for (KBr + KI) > (KCl + KI) > (KCl + KBr).

(3) An enhancement in the structure breaking efficiency of Cl\(^-\), Br\(^-\) and I\(^-\) has been observed in the presence of K\(^+\) ion and the enhancement is found to be in the order I\(^-\) > Br\(^-\) > Cl\(^-\).

(4) The structural contribution to the shift in TSVM, \(\Delta T_{str}\), is found to vary linearly with ionic strength of the mixed electrolyte solution reflecting that the effect of K\(^+\) on the structural propensities of Cl\(^-\), Br\(^-\) and I\(^-\) would remain the same even at constant ionic strength. However, further studies on mixed electrolytic solutions at constant ionic strength are essential to delineate the structural effects of anions and cations and would be taken up.

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