Effect of ammonium halides on the temperature of sound velocity maximum of water

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Effect of ammonium halides on the temperature of sound velocity maximum (TSVM) of water 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 °C intervals over a range of ±5 °C to either side of the TSVM of the solutions. The accuracy in fixing the TSVM is ± 0.2 °C. The shift in TSVM of water due to the addition of the NH₄Cl, ΔTSVM is found to be positive up to w = 3.4 x 10⁻² and negative thereafter, where w represents weight fraction of the solute. The shifts in TSVM of water due to the addition of NH₄Br and NH₄I are found to be negative throughout the concentration range. The structural contribution to the shift in TSVM of water, ΔTSVM, is found to be positive for NH₄Cl and increases with increase in the concentration non-linearly. ΔTSVM for NH₄Br is almost zero up to w = 3 x 10⁻² and thereafter becomes negative. ΔTSVM for NH₄I is found to be negative throughout the concentration range. The results are explained in terms of the structure, making and breaking nature of anions and cations present in the solutions.

1 Introduction

Water exhibits a maximum in its sound velocity versus temperature plot at 74 °C, which can be explained on the basis of two-state model for water, common to many theories. At any given temperature, water can be considered to be an equilibrium mixture of structured (hydrogen-bonded and voluminous) and non-structured (non-hydrogen bonded and dense) species. At low temperatures, the structured form is predominant, while at high temperatures it is the non-structured form. A rise in temperature produces volume expansion of both species, which corresponds to a negative temperature coefficient of velocity. Superposed over this will be an equilibrium shift between the two species, resulting in an increase in the population of the non-hydrogen bonded, dense component, which corresponds to a positive temperature coefficient of sound velocity. The maximum in ultrasonic velocity versus temperature at 74 °C thus corresponds to the balance between these two opposing effects. The presence of a solute (electrolyte or non-electrolyte) changes the structure of water, affecting the temperature of the sound velocity maximum (TSVM). Solutes may be classified as structure makers or structure breakers, depending on whether the shift in TSVM is towards higher or lower temperatures.

Tamm & Haddenhorst, Mikhailov et al., Marks, Pancholy & Singal and Gnanamba & Ramachandra Rao have studied the effect of different electrolytes on TSVM. In these investigations, the accuracy in fixing TSVM is less and ranged from ± 2 to ± 5 °C. Because of these large errors in fixing TSVM, there is ambiguity in delineating the structural properties of the ions. Subrahmanyam & Raghavan studied for the first time, the effect of LiCl, LiBr, LiI, NaCl, KCl and RbCl on the TSVM of water by measuring ultrasonic velocity with a higher degree of accuracy (± 0.003 %) and the accuracy in fixing TSVM was ±0.2 °C. This enabled them to delineate the structure, promoting and disrupting nature of the ions, unambiguously. Subrahmanyam & Sivakumar studied the effect of LiOH on the TSVM of water and Achari et al. studied the effect of lithium carbonate, ammonium phosphate, ammonium acetate and strontium phosphate on TSVM of water. The effect of alkali fluorides, iodides, acetates, formates and nitrates on TSVM of water have been studied by Sivakumar. The effect of sulphates of lithium, sodium, potassium,
ammonium and magnesium on the TSVM of water have been studied by Venkata Ramana et al.\textsuperscript{17}

In the present work, the authors studied the effect of ammonium halides on TSVM of water with improved accuracy in fixing TSVM, so as to delineate more precisely the structural properties of ammonium and halide ions, since there exists ambiguity due to large errors in fixing TSVM for these solutions\textsuperscript{18,19}. The results are presented in this paper.

Fig. 1 — Ultrasonic velocity ($v$) versus temperature ($t$) in aqueous ammonium chloride at different weight fractions [A. Pure water; B. $w = 0.0092$; C. $w = 0.0150$; D. $w = 0.0232$; E. $w = 0.0371$; F. $w = 0.0482$; G. $w = 0.0658$]

2 Experimental Details

Ultrasonic velocities in water and dilute aqueous solutions of NH$_4$Cl, NH$_4$Br and NH$_4$I were determined using a single crystal variable-path interferometer designed and fabricated in our laboratory. A tri-tet crystal-controlled oscillator with frequency stability $\pm 1$ Hz was used to excite the quartz transducer. The transducer, whose fundamental frequency is 1 MHz, is excited at its third harmonic. The frequency was measured with a digital frequency meter with an accuracy of one part per million. The voltage variations across the transducer were observed using a difference-amplifier followed by an electronic voltmeter.

The mechanical assembly of the interferometer (designed and fabricated in the laboratory) was immersed in a thermostatic water bath whose temperature can be controlled up to $\pm 0.01$ °C, using suitable permanent heaters followed by on-off low wattage heaters. Stirring it periodically, minimized the temperature gradients inside the experimental liquid. The temperature of the interferometric liquid, measured using a bead type thermostat which forms one arm of a constant current Wheatstone bridge followed by a chopper-stabilized operational amplifier as null detector, was found to be constant within $\pm 0.005$ °C. The thermostat and the electronic assembly were housed in an air-conditioned room, whose temperature was maintained at $20 \pm 1$ °C. This resulted in improved stability of the crystal oscillator and the efficiency of the temperature control. The reflector of the interferometer is moved by a specially designed screw, incorporated in the interferometer, which can be read to an accuracy of $\pm 1 \times 10^{-2}$ mm. The path length was measured for 50 dips and this resulted in measurement of wavelength of the ultrasonic beam with an accuracy of $\pm 0.0025\%$. The high degree of accuracy with which the frequency of the transducer was measured, and the temperature stability of the interferometric liquid and accuracy in the measurement of the path length resulted in measurement of ultrasonic velocity in the experimental solution with an accuracy of $\pm 0.003\%$.

The interferometer was calibrated by measuring ultrasonic velocity in triple distilled de-gassed water. At each temperature, six to eight measurements were taken and the average is chosen as the ultrasonic velocity, which is found to be accurate to $\pm 0.05$ ms$^{-1}$. The standard deviation of ultrasonic data at any given temperature estimated is found to be $\pm 0.04$ ms$^{-1}$. This accuracy could be realized due to the fact that, the temperature coefficient of ultrasonic velocity in dilute aqueous solution of electrolytes is extremely small apart from the accuracies involved in the measurement of path length and frequency of the transducer.

3 Results and Discussion

The measured ultrasonic velocities in aqueous solutions of NH$_4$Cl, NH$_4$Br and NH$_4$I, as a function of temperature, 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 and hence a transparent template of the ultrasonic velocity-temperature curve for pure water was used to fix the TSVM of the solutions. The accuracy in fixing TSVM is ±0.2°C.

![Graph showing ultrasonic velocity vs temperature for aqueous ammonium bromide solutions](image)

The shift observed in the temperature of sound velocity maximum of water caused by the addition of an electrolyte of certain weight is given by:

$$\Delta T_{obs} = T_s - T_w = T_s - T_{w2}$$  \hspace{1cm} \text{(1)}

where $T_s$ and $T_w$ represent the TSVM of an aqueous electrolyte solution and water, respectively.

This shift may be thought of as arising due to two effects, namely, the dilution effect and the structural effect. The structural effect arises as a result of interaction between solute and solvent. It will be positive if the hydrogen-bonded structure of water is stabilized by the solute and negative if the hydrogen-bonded structure is destabilized by the presence of solute, creating monomers of water molecules. The dilution effect arises merely due to dissolution of the electrolyte in water and is always towards shifting TSVM of water to lower temperatures. To separate these two effects, it is necessary to evaluate the effect of dilution on the TSVM of water by the addition of the solute. This can be done by combining the expressions representing the temperature dependence of sound velocity in water and in the solute.

![Graph showing ultrasonic velocity vs temperature for aqueous ammonium iodide solutions](image)
where $u_2^0$ and $\alpha_s$ represent the velocity of sound in the solute at 0 °C and temperature coefficient of sound velocity in the solute, respectively.

Fig. 4 — Variation of $u_2^0$ and $\alpha_s$ with molecular weight (M) of NH$_4$Cl, NH$_4$Br and NH$_4$I

According to Willard$^2$ the temperature dependence of sound velocity in pure water conforms to the relation:

$$u_t = 1557 - 0.0245 (74 - T)^2$$

where $t$ represents the temperature in °C. The temperature dependence of sound velocity in the solute can be represented by:

$$u_t = u_2^0 - \alpha_s T$$

where $u_t$ represents the velocity of sound in the solution.

Substituting Eqs (2) and (3) in Eq. (4), one can get:

$$u_t^0 = (1 - w) u_1^0 + w u_2^0 + w \alpha_s T$$

Differentiating Eq. (5) with respect to temperature and making use of the condition that:

$$[1557 - 0.0245 (74 - T)^2] 0.049 (74 - T)$$

one can get:

$$\left( \frac{du_t}{dT} \right)_{T=T_s} = b (u_2^0 - \alpha_s T_s) \alpha_s$$

where $b = \left( \frac{w}{1 - w} \right)$.
The term within the square brackets in Eq. (6) represents the velocity of sound in water at temperature of sound velocity maximum in solution, and it can be replaced by 1557 m s\(^{-1}\) if \(T\) did not differ appreciably from 74 °C. Hence:

\[
(1557)(0.049)(74 - T_i) = b (u_2^0 - \alpha_u T_i)
\]

Simplifying, one can get:

\[
T_i = \frac{5646 - b \alpha_u u_2}{76.3 - b \alpha_u} \quad ...(8)
\]

If there is no change in the structure of water due to the addition of an electrolyte, then, \(T_i\) given by Eq. (8) represents the ideal value of the temperature of sound velocity maximum in the solution. That is:

\[
T_i = (T_{i,i}) \quad ...(9)
\]

If the hydrogen-bonded structure of water is modified by presence of the solute, then, the TSVM observed experimentally \((T_{i,ex})\) will differ from that of the ideal value \((T_{i,i})\). Hence, the structural contribution to the shift in TSVM of water due to addition of the solute is given by:

\[
\Delta T_{i,w} = (T_{i,ex}) - (T_{i,i}) \quad ...(10)
\]

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

To calculate \((T_{i,w})\), one needs \(u_2^0\) and \(\alpha_u\), which can be evaluated from data on the temperature dependence of the elastic constants. Since the solutes used are solid electrolytes, one can have three velocities associated with sound wave propagation, one longitudinal and two transverse. Since there is no reason to prefer any one of these velocities, one may use the mean velocity \(u_w\) for \(u_2\) in the electrolytes, given by:

\[
u_2 = u_w = \left[\frac{1}{3} \left(\frac{1}{u_1^0} + \frac{2}{u_2^0}\right)\right]^{1/3}
\]

where \(u_1\) and \(u_2\) represent the longitudinal and transverse wave velocities in the polycrystalline aggregates of the electrolytes. It may be mentioned here that, to evaluate the Debye characteristic temperature of polycrystalline samples, the average velocity normally used is that given by Eq. (11) and the authors' preference to use \(u_w\) instead of either \(u_1\) or \(u_2\) to evaluate \((T_{i,w})\) is reasonable.

The mean velocities of sound \((u_2)\) in the solutes (NH\(_4\)Cl and NH\(_4\)Br) at different temperatures have been evaluated making use of the data of elastic constants and their temperature dependence\(^{22}\). The method followed to calculate \(u_1\) and \(u_2\) from elastic constant data, necessary to evaluate \(u_w\), making use of Eq. (11), is detailed in an earlier communication\(^{22}\). By least square-fitting of \(u_2\) versus temperature data to Eq. (3), \(u_2^0\) and \(\alpha_u\) have been evaluated. \(u_2^0\) and \(\alpha_u\) for NH\(_4\)Cl and NH\(_4\)Br are 3011 m s\(^{-1}\), 0.82 m s\(^{-1}\) K\(^{-1}\) and 2189 m s\(^{-1}\), 0.57 m s\(^{-1}\) K\(^{-1}\), respectively. It was not possible to evaluate \(u_1^0\) and \(\alpha_u\) for NH\(_4\)I, since the data on temperature dependence of its elastic constants are not available in literature. However, considering that \(u_2^0\) and \(\alpha_u\) vary linearly with molecular weight, these values for NH\(_4\)I have been evaluated by extrapolating the curves as shown in Fig. 4. The values of \(u_2^0\) and \(\alpha_u\) obtained graphically for NH\(_4\)I are 1320 m s\(^{-1}\) and 0.30 m s\(^{-1}\) K\(^{-1}\), respectively. These values are only a rough estimate, in the absence of experimental data and the authors have used these values to calculate \((T_{i,w})\) to get an idea about the structural contribution.
Table 1: Values of $(T_{\text{exp}})$, $(T_{\text{th}})$, $\Delta T_{\text{obs}}$, and $\Delta T_{\text{th}}$ for halides of ammonium at different weight fractions of ammonium halides.

<table>
<thead>
<tr>
<th>$w$</th>
<th>$(T_{\text{exp}})$ (°C)</th>
<th>$(T_{\text{th}})$ (°C)</th>
<th>$\Delta T_{\text{obs}}$ (°C)</th>
<th>$\Delta T_{\text{th}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>74.0 ± 0.2</td>
<td>74.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.0092</td>
<td>74.3 ± 0.2</td>
<td>73.7 ± 0.2</td>
<td>+0.6 ± 0.2</td>
<td>+0.6 ± 0.2</td>
</tr>
<tr>
<td>0.0150</td>
<td>74.2 ± 0.2</td>
<td>73.5 ± 0.2</td>
<td>+0.7 ± 0.2</td>
<td>+1.1 ± 0.2</td>
</tr>
<tr>
<td>0.0232</td>
<td>74.3 ± 0.2</td>
<td>73.2 ± 0.2</td>
<td>+1.1 ± 0.2</td>
<td>+1.1 ± 0.2</td>
</tr>
<tr>
<td>0.0371</td>
<td>73.9 ± 0.2</td>
<td>72.8 ± 0.2</td>
<td>+1.1 ± 0.2</td>
<td>+1.1 ± 0.2</td>
</tr>
<tr>
<td>0.0482</td>
<td>73.9 ± 0.2</td>
<td>72.3 ± 0.2</td>
<td>+1.6 ± 0.2</td>
<td>+1.6 ± 0.2</td>
</tr>
<tr>
<td>0.0658</td>
<td>73.7 ± 0.2</td>
<td>71.8 ± 0.2</td>
<td>+1.9 ± 0.2</td>
<td>+1.9 ± 0.2</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>73.9 ± 0.2</td>
<td>74.0 ± 0.2</td>
<td>-0.1 ± 0.2</td>
<td>-0.1 ± 0.2</td>
</tr>
<tr>
<td>0.0015</td>
<td>73.7 ± 0.2</td>
<td>73.7 ± 0.2</td>
<td>0.0 ± 0.2</td>
<td>0.0 ± 0.2</td>
</tr>
<tr>
<td>0.0208</td>
<td>73.5 ± 0.2</td>
<td>73.5 ± 0.2</td>
<td>0.0 ± 0.2</td>
<td>0.0 ± 0.2</td>
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<tr>
<td>0.0293</td>
<td>73.5 ± 0.2</td>
<td>73.5 ± 0.2</td>
<td>0.0 ± 0.2</td>
<td>0.0 ± 0.2</td>
</tr>
<tr>
<td>0.0449</td>
<td>73.0 ± 0.2</td>
<td>73.2 ± 0.2</td>
<td>-0.2 ± 0.2</td>
<td>-0.2 ± 0.2</td>
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<tr>
<td>0.0553</td>
<td>72.9 ± 0.2</td>
<td>73.1 ± 0.2</td>
<td>-0.2 ± 0.2</td>
<td>-0.2 ± 0.2</td>
</tr>
<tr>
<td>0.0666</td>
<td>72.5 ± 0.2</td>
<td>72.9 ± 0.2</td>
<td>-0.4 ± 0.2</td>
<td>-0.4 ± 0.2</td>
</tr>
<tr>
<td>NH$_4$Br</td>
<td>73.8 ± 0.2</td>
<td>74.0 ± 0.2</td>
<td>-0.2 ± 0.2</td>
<td>-0.2 ± 0.2</td>
</tr>
<tr>
<td>0.0056</td>
<td>73.5 ± 0.2</td>
<td>73.5 ± 0.2</td>
<td>-0.2 ± 0.2</td>
<td>-0.2 ± 0.2</td>
</tr>
<tr>
<td>0.0120</td>
<td>73.5 ± 0.2</td>
<td>73.5 ± 0.2</td>
<td>-0.2 ± 0.2</td>
<td>-0.2 ± 0.2</td>
</tr>
<tr>
<td>0.0179</td>
<td>73.5 ± 0.2</td>
<td>73.9 ± 0.2</td>
<td>-0.6 ± 0.2</td>
<td>-0.6 ± 0.2</td>
</tr>
<tr>
<td>0.0220</td>
<td>73.0 ± 0.2</td>
<td>73.9 ± 1.0 ± 0.2</td>
<td>-0.9 ± 0.2</td>
<td>-0.9 ± 0.2</td>
</tr>
<tr>
<td>0.0322</td>
<td>72.3 ± 0.2</td>
<td>73.8 ± 1.7 ± 0.2</td>
<td>-1.5 ± 0.2</td>
<td>-1.5 ± 0.2</td>
</tr>
<tr>
<td>NH$_4$I</td>
<td>73.8 ± 0.2</td>
<td>74.0 ± 0.2</td>
<td>-0.2 ± 0.2</td>
<td>-0.2 ± 0.2</td>
</tr>
</tbody>
</table>

The values of $\Delta T_{\text{obs}}$ as a function of weight fraction ($w$) of NH$_4$Cl, NH$_4$Br and NH$_4$I are presented graphically in Fig. 5. An examination of the data presented in Fig. 5 indicates that, $\Delta T_{\text{obs}}$ for NH$_4$Cl is positive up to $w \approx 3.4 \times 10^2$ and negative, thereafter. Value of $\Delta T_{\text{obs}}$ is negative for NH$_4$Br and NH$_4$I and the negative shift increases with increase in the concentration of these electrolytes. The values of $\Delta T_{\text{th}}$ for NH$_4$Cl, NH$_4$Br and NH$_4$I are presented graphically in Fig. 6. $\Delta T_{\text{th}}$ is positive for NH$_4$Cl and increases with increase in the concentration non-linearly. Value of $\Delta T_{\text{th}}$ for NH$_4$I is almost zero, up to $w \approx 3 \times 10^2$ and thereafter become negative. Value of $\Delta T_{\text{th}}$ for NH$_4$I is negative throughout the concentration range and $\Delta T_{\text{th}}$ versus $w$ is parabolic nature.

Namuro and Endo[18,19] have studied the variation of ultrasonic velocity as a function of temperature in aqueous solutions of NH$_4$I, NH$_4$Br and NH$_4$I in the temperature range 55-85 °C. They reported that, the velocity-peak temperature remains sensibly constant up to 4.5 mole %, independent of the kinds of anions for all the ammonium halides and the behaviour for high concentrations beyond 4.5 mole % is quite different according to the kinds of halogen ions. Beyond 4.5 mole % the velocity-peak temperature remains sensibly constant for ammonium bromide at 74 °C and in the case of ammonium iodide, it decreases initially and subsequently increase with concentration. They stated that the ionic radius is smaller for Cl (1.81 Å), larger for I (2.16 Å) and intermediate for Br (1.95 Å), corresponding to the difference in the tendencies of velocity-peak temperature versus concentration curves for these substances.
NH$_4^+$ and Br are comparatively equal and hence, one can observe almost zero or a very small negative shift. In aqueous solutions of NH$_4$I, the structure-breaking nature of I dominates over the structure-promoting nature of NH$_4^+$ and hence, one can observe $\Delta T_m$ to be negative and increasing with increase in the concentration of NH$_4$I. The stabilization of the hydrogen structure of water by NH$_4^+$ may be considered to be due to filling up of cavities in network sites of water as is evidenced from X-ray scattering data$^{21-23}$.

At any given concentration, $\Delta T_m$ for NH$_4$Cl $>$ NH$_4$Br $>$ NH$_4$I indicating the structure-breaking nature of I $>$ Br $>$ Cl. It may be mentioned here that, this is the order found for structure-breaking nature of these ions from viscosity B-coefficient$^8$ and activation energy of viscous flow data$^{24}$. The viscosity B-coefficient for Cl, Br and I, respectively are, $-0.007$, $-0.042$ and $-0.068$. The negative values indicate their structure-breaking character and the magnitudes indicate the strength of structure-breaking property of Cl, Br and I.

4 Conclusions
1. The present study indicates that, NH$_4^+$ is a structure-promoting ion while Cl, Br and I are structure-disrupting ions.
2. The structure-disrupting property of Cl, Br and I lies in the order Cl $<$ Br $<$ I.
3. The observed velocity-peak temperature is slightly higher than 74 °C up to $W = 4 \times 10^2$ for NH$_4$Cl and less than 74 °C for NH$_4$Br and NH$_4$I. This observation is quite contrary to the observation made by Namoto & Endo$^{21,22}$.
4. Evaluation of structural contribution to the shift in TSVM of water enabled the delineation of structural propensities of NH$_4^+$, Cl, Br and I in aqueous solutions of halides of ammonium unambiguously, as compared to the studies made by Namoto & Endo$^{21,22}$.

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References