

CHAPTER 4

DISCUSSION OF RESULTS

4.1 Theoretical aspects - Derivation of the expression for the shift in the temperature of sound velocity maximum in water due to the addition of an electrolyte

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

$$\Delta T_{\text{obs}} = (T_s - T_w) = (T_s - 74) \quad \dots \quad 4.1.1$$

where T_s and T_w represent the TSVM of aqueous electrolyte solution and water respectively. This shift may be thought of as arising due to two effects namely dilution effect and the 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 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 the 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 solute. This can be done by combining the expressions representing the temperature dependence of sound velocity in water and in the solute.

According to Willard [123] the temperature dependence of sound velocity in pure water conforms to the relation

$$u_1 = 1557 - 0.0245 (74 - t)^2 \quad \dots \quad 4.1.2$$

where 't' represents the temperature in °C.

The temperature dependence of sound velocity in the solute can be represented by

$$u_2 = u_2^{\circ} - \alpha t \quad \dots \quad 4.1.3$$

where u_2° and α represent the velocity of sound in the solute at 0°C and temperature coefficient of sound velocity in the solute respectively.

Assuming additivity of internal energy, the velocity of sound in an electrolyte solution can be written as [124]

$$u^2 = (1 - w) u_1^2 + w u_2^2 \quad \dots \quad 4.1.4$$

where w represents the weight fraction of the solute in the solution.

Substituting Eqns. 4.1.2 and 4.1.3 in Eqn. 4.1.4, we get

$$u^2 = (1 - w) [1557 - 0.0245 (74 - t)^2]^2 + w (u_2^{\circ} - \alpha t)^2 \quad \dots \quad 4.1.5$$

Differentiating the above expression with respect to temperature and making use of the condition that

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

$$[1557 - 0.0245 (74 - T_s)^2] 0.049 (74 - T_s) = b (u_2^{\circ} - \alpha T_s)^2 \alpha \quad \dots \quad 4.1.6$$

$$\text{where } b = \left(\frac{w}{1 - w} \right)$$

The term within the square brackets in Eqn. 4.1.6 represents the velocity of sound in water at the temperature of sound velocity maximum in the solution and can be replaced by 1557 if T_s does not differ appreciably from 74°C. Hence

$$(1557) (0.049) (74 - T_s) = b (u_2^\circ - \alpha T_s) \alpha \quad \dots \quad 4.1.7$$

$$T_s = \frac{5646 - b \alpha u_2^\circ}{76.3 - b \alpha^2} \quad \dots \quad 4.1.8$$

If there is no change in the structure of water due to the addition of the electrolyte, then T_s given by Eqn. 4.1.8 represents the ideal value of the temperature of sound velocity maximum in the solution. That is

$$T_s = (T_s)_{id} \quad \dots \quad 4.1.9$$

If the hydrogen bonded structure of water is modified by the presence of the solute, 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 solute is given by

$$\Delta T_{str} = (T_s)_{exp} - (T_s)_{id} \quad \dots \quad 4.1.10$$

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

To calculate $(T_s)_{id}$, we need u_2° and α . u_2° and α 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 velocity u_m for u_2 in the electrolytes given by the following relation

$$u_m = u_2 = \left[\frac{1}{3} \left(\frac{1}{u_l^3} + \frac{2}{u_t^3} \right) \right]^{-1/3} \quad \dots \quad 4.1.11$$

where u_l and u_t 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 the one given by Eqn. 4.1.11 and our preference to use u_m instead of either u_l or u_t to evaluate $(T_s)_{id}$ is reasonable. u_2° and α for the electrolytes have been evaluated making use of the data on elastic constants and their temperature dependence for the electrolytes for which literature data are available out of the electrolytes studied in the present work. The observed shift ΔT_{obs} and the structural shift ΔT_{str} are evaluated using Eqn. 4.1.1 and Eqns. 4.1.8 and 4.1.10 respectively.

4.2 Effect of sulphates of lithium, sodium, potassium, magnesium and ammonium on the temperature of sound velocity maximum of water

u_2^0 and α for $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 have been evaluated making use of the data on elastic constants and their temperature dependence[125]. The values of u_2^0 and α for $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 respectively are 2518 m s^{-1} , $0.14 \text{ m s}^{-1} \text{ }^\circ\text{C}^{-1}$ and 2851 m s^{-1} , $0.58 \text{ m s}^{-1} \text{ }^\circ\text{C}^{-1}$. The author could not evaluate u_2^0 and α for Li_2SO_4 , Na_2SO_4 and MgSO_4 due to nonavailability of elastic constants data in the literature at higher temperatures.

The values of T_s and ΔT_{obs} at different concentrations of the electrolytes are presented in Table 4.2.1. The $(T_s)_{\text{id}}$ and ΔT_{str} for $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 evaluated using Eqns. 4.1.8 and 4.1.10 as discussed in Section 4.1 are also given in this table. The values of ΔT_{obs} as a function of weight fraction (w) of Li_2SO_4 , Na_2SO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and MgSO_4 are presented graphically in Fig. 4.2.1. The values of ΔT_{str} for $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 as a function of weight fraction are presented graphically in Fig. 4.2.2. An examination of the data presented in Fig. 4.2.1 indicates that ΔT_{obs} for Li_2SO_4 and MgSO_4 are positive at low concentrations and respectively becoming maximum around $w \simeq 0.5 \times 10^{-2}$ and 1×10^{-2} . ΔT_{obs} for Li_2SO_4 and MgSO_4 become negative respectively beyond $w \simeq 2.7 \times 10^{-2}$ and 2×10^{-2} . ΔT_{obs} values for Na_2SO_4 , K_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ are negative and the negative shift increases with increase in the concentration of the electrolytes.

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Table 4.2.1 $(T_s)_{\text{exp}}$, $(T_s)_{\text{id}}$, ΔT_{obs} , and ΔT_{str} at different weight fractions of sulphates of lithium, sodium, potassium, ammonium and magnesium

w	$(T_s)_{\text{exp}}$ (°C)	$(T_s)_{\text{id}}$ (°C)	ΔT_{obs} (°C)	ΔT_{str} (°C)
0.0000	74.0	74.0	0.00	0.000
Li_2SO_4				
0.0061	74.9		+0.9	
0.0105	74.5		+0.5	
0.0220	74.1		+0.1	
0.0328	73.8		-0.2	
0.0424	73.1		-0.9	
0.0590	72.0		-2.0	
0.0783	70.8		-3.2	
Na_2SO_4				
0.0141	73.4		-0.6	
0.0250	72.2		-1.8	
0.0332	70.9		-3.1	
0.0471	69.8		-4.2	
0.0563	69.1		-4.9	
0.0680	68.1		-5.9	
K_2SO_4				
0.0123	73.3	73.7	-0.7	-0.4
0.0201	71.8	73.6	-2.2	-1.8
0.0319	70.0	73.3	-3.9	-3.3
0.0425	69.0	73.1	-5.0	-4.1
0.0556	68.2	72.8	-5.8	-4.6
0.0631	67.1	72.6	-6.9	-5.5
$(\text{NH}_4)_2\text{SO}_4$				
0.0090	73.5	74.0	-0.5	-0.5
0.0203	72.9	73.9	-1.1	-1.0
0.0301	72.0	73.9	-2.0	-1.9
0.0434	71.1	73.8	-2.9	-2.7
0.0511	70.0	73.8	-4.0	-3.8
0.0681	68.9	73.7	-5.1	-4.8
MgSO_4				
0.0071	74.3		+0.3	
0.0144	74.3		+0.3	
0.0213	73.7		-0.3	
0.0372	73.0		-1.0	
0.0480	71.6		-2.4	
0.0601	71.1		-2.9	
0.0720	69.5		-4.5	

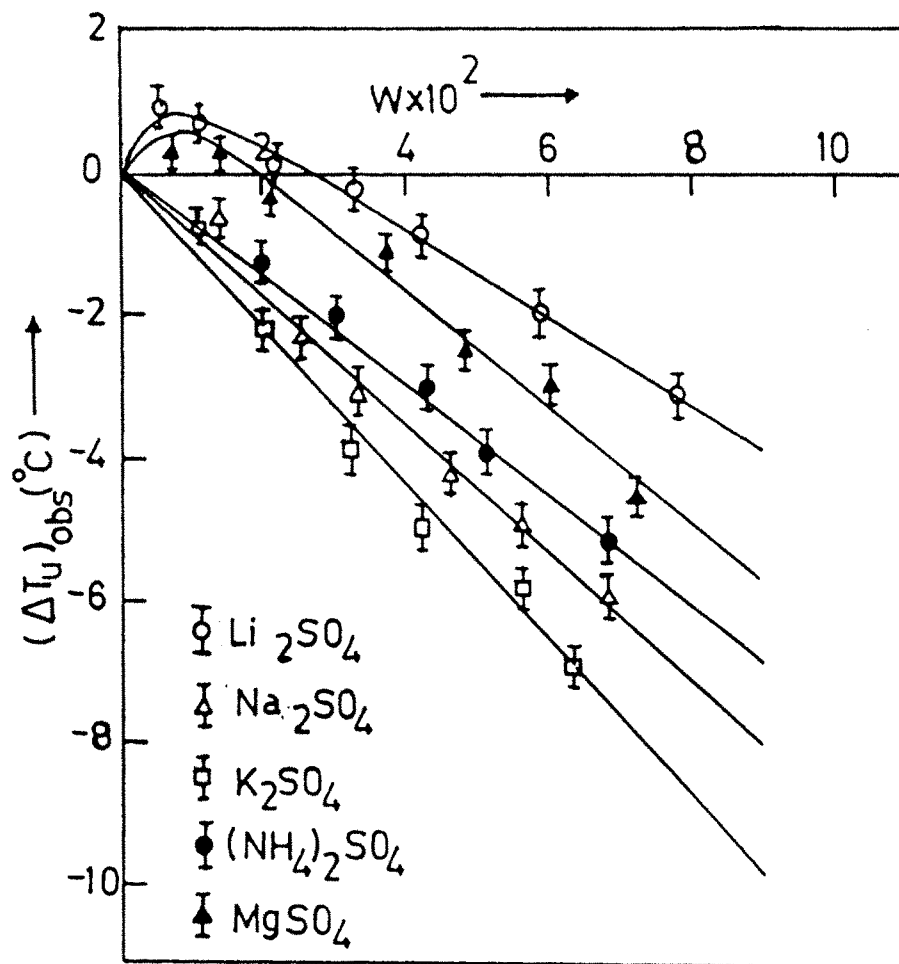


Fig. 4.2.1: ΔT_{obs} versus weight fraction of sulphates of lithium, sodium, potassium, magnesium and ammonium.

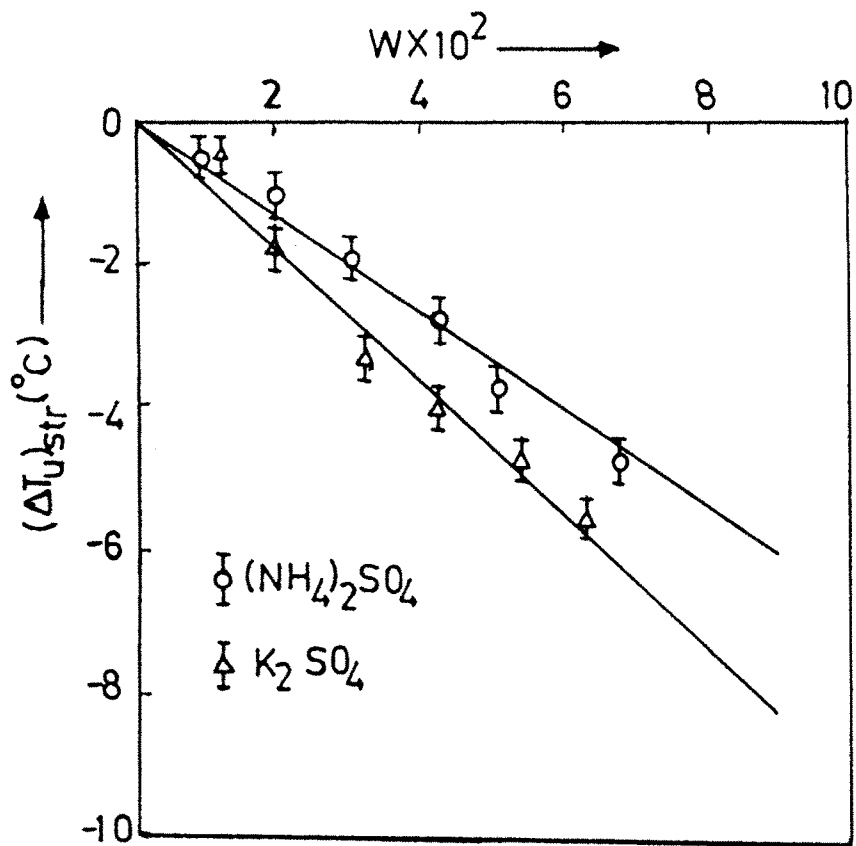


Fig. 4.2.2: ΔT_{str} versus weight fraction of ammonium sulphate and potassium sulphate.

The viscosity B-coefficient [126] and the activation energy of viscous flow data [127] classify Na^+ as a structure ordering ion. The studies carried out on the effect of NaCl on TSVM of water [16] indicate Na^+ as a structure promoter. In the present work, we find ΔT_{obs} is negative for Na_2SO_4 indicating SO_4^{2-} as strong structure breaker. The positive shift observed for Li_2SO_4 indicates that Li^+ as a strong structure promoter and the observation is in confirmity with the studies carried out by Subrahmanyam and Raghavan [16] on the effect of lithium halides on TSVM of water. The strong structure promoting nature of Li^+ is also evident from the large positive viscosity B-coefficient accompanied by the largest loss of entropy [126].

The positive shift observed at low concentrations for MgSO_4 indicates that Mg^{2+} promotes the hydrogen bonded structure of water. The maximum observed in ΔT_{obs} versus w for Li_2SO_4 and MgSO_4 may be considered to be due to the stabilization of hydrogen bonded clusters by Li^+ and Mg^{2+} ions against thermal collapse and also overcoming the disruptive effect of SO_4^{2-} ions. Beyond these optimum concentrations the structure breaking nature of SO_4^{2-} dominates and at $w \simeq 2.7 \times 10^{-2}$ and 2×10^{-2} where ΔT_{obs} is zero respectively for Li_2SO_4 and MgSO_4 , the structure promoting nature of Li^+ and Mg^{2+} are counter balanced by SO_4^{2-} ions. At higher concentrations of these electrolytes, the structure breaking nature of SO_4^{2-} ion dominates the structure promoting nature of Li^+ and Mg^{2+} resulting in ΔT_{obs} negative.

Enthalpy studies for common ion mixtures [128,129] indicate Li^+ and Mg^{2+} as structure promoting ions whereas K^+ as structure breaking ion. The present studies as can be seen from Fig. 4.2.1 are in conformity with the above observation except in the case of $(\text{NH}_4)_2\text{SO}_4$ where ΔT_{obs} is negative throughout the concentration range. The structure promoting nature of NH_4^+ is not seen. This is further confirmed from the data of the structural contribution to the shift in TSVM due to the addition of $(\text{NH}_4)_2\text{SO}_4$. This indicates that the structure stabilization by NH_4^+ ion is more than counter balanced by the structure breaking SO_4^{2-} ion. ΔT_{str} for K_2SO_4 is negative and increases with increase in the concentration of K_2SO_4 confirming the structure disruptive nature of K^+ .

At any given concentration, ΔT_{str} for $\text{Li}_2\text{SO}_4 > \text{MgSO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{K}_2\text{SO}_4$ and ΔT_{str} for $(\text{NH}_4)_2\text{SO}_4 > \text{K}_2\text{SO}_4$ indicating that the structure promoting nature of $\text{Li}^+ > \text{Mg}^{2+}$ and structure breaking nature of $\text{K}^+ > \text{Na}^+ > \text{NH}_4^+$. This observation is consistent with the order found for alkali metal ions observed from the studies on the effect of alkali-halides on TSVM of water [16].

4.3 Effect of chlorides of magnesium, calcium, strontium and barium on the temperature of sound velocity maximum of water

The temperature of sound velocity maximum T_s and ΔT_{obs} at different weight fractions of MgCl_2 , CaCl_2 , SrCl_2 and BaCl_2 are presented in Table 4.3.1. Due to non-availability of experimental data on the temperature dependence of elastic constants of MgCl_2 , CaCl_2 , SrCl_2 and BaCl_2 in the literature, the author could not evaluate the values of T_{id} and hence the structural shifts. ΔT_{obs} versus weight fraction w , of MgCl_2 , CaCl_2 , SrCl_2 and BaCl_2 are presented graphically in Fig. 4.3.1. An examination of the data presented in Fig. 4.3.1 indicates that the values of ΔT_{obs} for MgCl_2 and CaCl_2 are positive at low concentrations becoming maximum around $w \simeq 2.3 \times 10^{-2}$ for MgCl_2 and $w \simeq 1.9 \times 10^{-2}$ for CaCl_2 and become negative around $w \simeq 5.6 \times 10^{-2}$ for MgCl_2 and $w \simeq 3.8 \times 10^{-2}$ for CaCl_2 . The positive shift observed at low concentrations for MgCl_2 and CaCl_2 indicate that Mg^{2+} and Ca^{2+} promote the hydrogen bonded structure of water and at high concentrations the conditions are not quite favourable for stabilization of water structure. In the entire concentration range studied, ΔT_{obs} for SrCl_2 and BaCl_2 are negative and increase with increase in the concentration. At any given concentration ΔT_{obs} for $\text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2 > \text{BaCl}_2$ indicating that the structural promoting nature of $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$.

It may be mentioned here that viscosity B-coefficient data [130] and activation energy of viscous flow [127] indicate Cl^- ion as structure breaker while the same data classify Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} ions as strong structure promoters. The viscosity

TABLE 4.3.1 $(T_s)_{\text{exp}}$ and ΔT_{obs} at different weight fractions of chlorides of magnesium, calcium, strontium and barium

w	$(T_s)_{\text{exp}}$ ($^{\circ}\text{C}$)	ΔT_{obs} ($^{\circ}\text{C}$)
0.0000	74.0	0.0
MgCl ₂		
0.0091	74.5	+0.5
0.0142	74.7	+0.7
0.0283	74.6	+0.6
0.0342	74.4	+0.4
0.0484	74.1	+0.1
0.0540	73.8	-0.2
0.0661	73.7	-0.3
CaCl ₂		
0.0142	74.2	+0.2
0.0257	74.2	+0.2
0.0351	73.9	-0.1
0.0440	73.7	-0.3
0.0536	73.3	-0.7
0.0646	73.0	-1.0
SrCl ₂		
0.0105	73.9	-0.1
0.0258	73.6	-0.4
0.0335	73.4	-0.6
0.0417	73.2	-0.8
0.0531	72.7	-1.3
0.0649	72.3	-1.7
BaCl ₂		
0.0151	73.6	-0.4
0.0243	73.1	-0.9
0.0309	72.9	-1.1
0.0415	72.5	-1.5
0.0553	71.9	-2.1
0.0690	71.3	-2.7

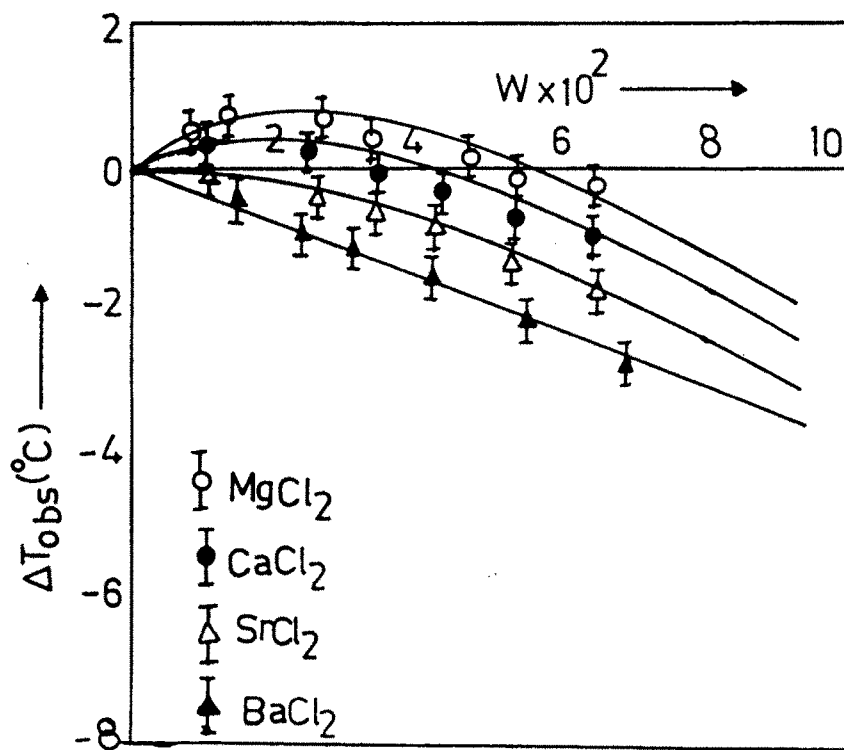


Fig. 4.3.1: ΔT_{obs} versus weight fraction of chlorides of magnesium, calcium, strontium and barium.

B-coefficient for Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} are 0.385, 0.285, 0.265 and 0.220 respectively at 25°C, indicating that the structure promoting capacity of these ions are in the order

$$\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$$

As per viscosity B-coefficient data even though Sr^{2+} and Ba^{2+} are structure-promoting ions, ΔT_{obs} for SrCl_2 and BaCl_2 are negative throughout the concentration range. Since it is not possible to evaluate structural contribution to the shift in TSVM due to paucity of data on the temperature dependence of elastic constants, one cannot come to the conclusion that Sr^{2+} and Ba^{2+} are not promoting the hydrogen bonded structure of water. However, the predominative effect of Cl^- in destabilization the structure of water can be effectively seen from the data of ΔT_{obs} being negative at all concentrations for SrCl_2 and BaCl_2 . It may be mentioned here that ΔT_{obs} for lithium acetate, sodium acetate and potassium acetate are found to be negative [17] even though the viscosity B-coefficients for acetate ion is +0.245 and viscosity B-coefficients for Li^+ , Na^+ and K^+ ions are +0.147, +0.086 and -0.007 at 25°C.

The present study shows that at high temperature (the range of temperatures where TSVM occurs) the viscosity B-coefficients for the ions may become negative indicating a structure-breaking propensity for these ions. It is a known fact that structure-promoting interactions are sensitive to temperature [131-134] and the ions which behave as structure promoters may turnout to be structure disrupters of high temperatures.

It may be mentioned here that the partial molal expansibilities [135] of the ions which promote the structure of water like Li^+ , NH_4^+ are negative and positive for structure breaking ions like Cl^- , Br^- and I^- . The partial molal expansibilities of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} are respectively -0.105, -0.042, -0.010 and -0.012. This data indicate that the structure promoting nature of these ions lies in the order

$$\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} \simeq \text{Ba}^{2+}$$

This is the trend reflected in the present TSVM studies also. At any given concentration ΔT_{obs} for $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$.

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

The values of the velocity of sound in the solute at 0°C (u_2^0) and temperature coefficient of sound velocity in the solute (α) for NH_4Cl and NH_4Br have been evaluated making use of data on elastic constants and their temperature dependence [125]. It has not been possible to evaluate u_2^0 and α for ammonium iodide as the data on temperature dependence of its elastic constants are not available in literature. u_2^0 and α for NH_4Cl and NH_4Br evaluated from temperature dependence of elastic constants data are 3011 m s^{-1} , $0.82 \text{ m s}^{-1} \text{ K}^{-1}$ and 2189 m s^{-1} , $0.57 \text{ m s}^{-1} \text{ K}^{-1}$ respectively. However considering that u_2^0 and α vary linearly with molecular weight, these values for NH_4I have been evaluated by extrapolating the curves as shown in Fig. 4.4.1. The u_2^0 and α values graphically obtained for NH_4I are 1320 m s^{-1} and $0.30 \text{ m s}^{-1} \text{ K}^{-1}$. These values are only a rough estimate in the absence of experimental data and the author has used these values to calculate T_{id} to get an idea about the structural contribution to the shift in TSVM. The values of structural contribution to the shift in TSVM of water, ΔT_{str} for NH_4Cl , NH_4Br and NH_4I are calculated according to the procedure described in Section 4.1. The values of $(T_{\text{s}})_{\text{exp}}$, ΔT_{obs} , $(T_{\text{s}})_{\text{id}}$ and ΔT_{str} for the three ammonium halides are presented in Table 4.4.1.

The values of ΔT_{obs} as a function of weight fraction (w) of NH_4Cl , NH_4Br and NH_4I are presented graphically in Fig. 4.4.2. An examination of the data presented in Fig. 4.4.2 indicates that ΔT_{obs} for NH_4Cl is positive up to $w \simeq 3.4 \times 10^{-2}$ and negative

Table 4.4.1 $(T_s)_{\text{exp}}$, $(T_s)_{\text{id}}$, ΔT_{obs} , and ΔT_{str} at different weight fractions of ammonium halides

w	$(T_s)_{\text{exp}}$ (°C)	$(T_s)_{\text{id}}$ (°C)	ΔT_{obs} (°C)	ΔT_{str} (°C)
0.0000	74.0	74.0	0.00	0.000
NH ₄ Cl				
0.0092	74.3	73.7	+0.3	+0.6
0.0150	74.2	73.5	+0.2	+0.7
0.0232	74.3	73.2	+0.3	+1.1
0.0371	73.9	72.8	-0.1	+1.1
0.0482	73.9	72.3	-0.1	+1.6
0.0658	73.7	71.8	-0.3	+1.9
NH ₄ Br				
0.0015	73.9	74.0	-0.1	-0.1
0.0208	73.7	73.7	-0.3	0.0
0.0293	73.5	73.5	-0.5	0.0
0.0449	73.0	73.2	-1.0	-0.2
0.0553	72.9	73.1	-1.1	-0.2
0.0636	72.5	72.9	-1.5	-0.4
NH ₄ I				
0.0056	73.8	74.0	-0.2	-0.2
0.0120	73.5	73.9	-0.5	-0.4
0.0179	73.3	73.9	-0.7	-0.6
0.0220	73.0	73.9	-1.0	-0.9
0.0322	72.3	73.8	-1.7	-1.5

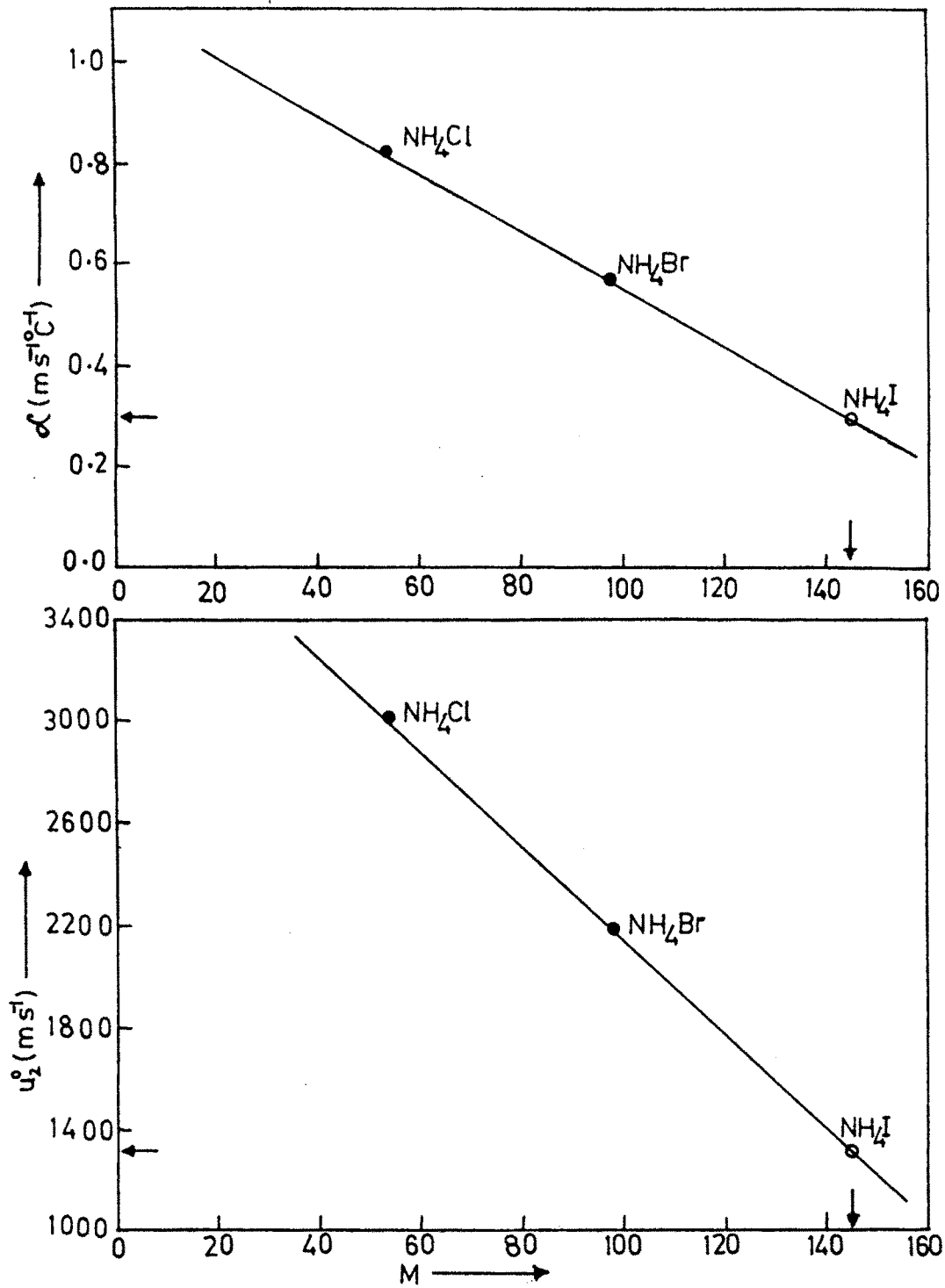


Fig. 4.4.1: u_2^0 and α versus molecular weight (M) of NH_4Cl , NH_4Br and NH_4I

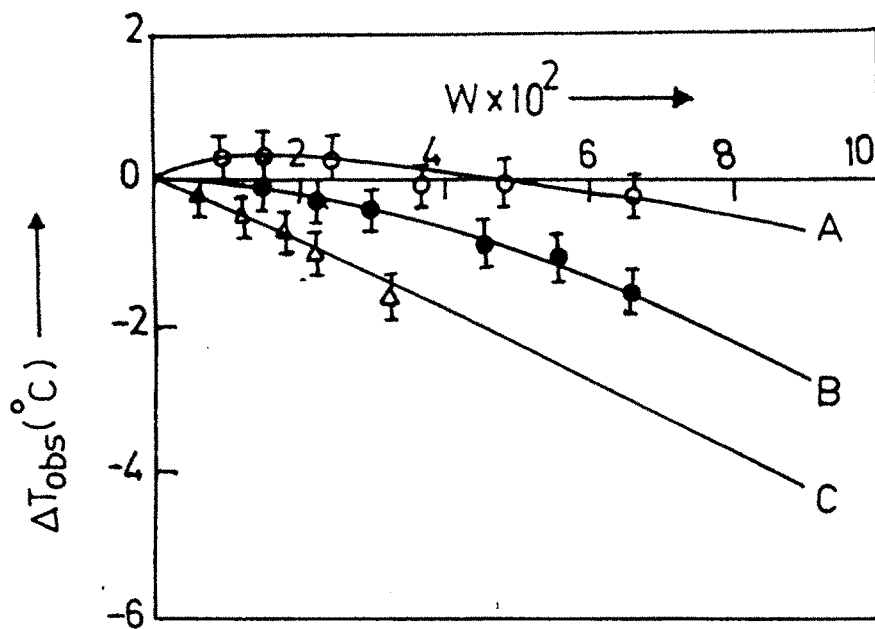


Fig.4.4.2

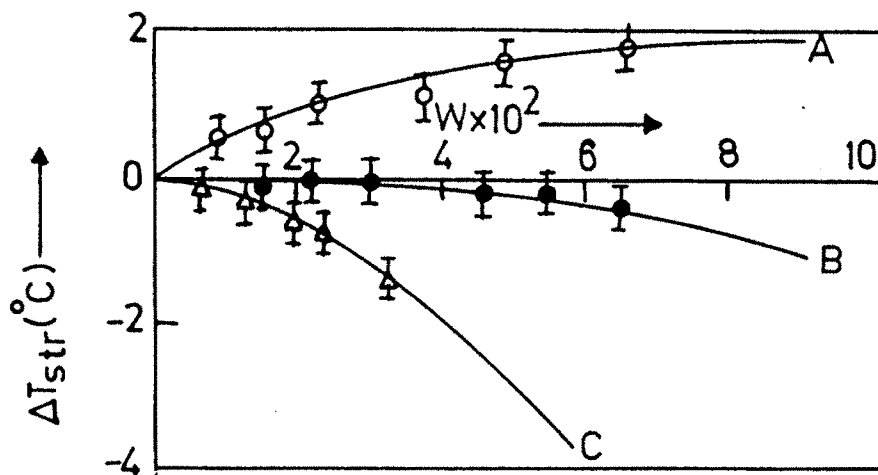


Fig.4.4.3

Fig. 4.4.2: ΔT_{obs} versus weight fraction of ammonium halides.

Fig. 4.4.3: ΔT_{str} versus weight fraction of ammonium halides.

- A \rightarrow ammonium chloride
- B \rightarrow ammonium bromide
- C \rightarrow ammonium iodide.

thereafter. The shift in TSVM, (ΔT_{obs}), is negative for NH_4Br and NH_4I and the negative shift increases with increase in the concentration of the electrolytes. The values of ΔT_{str} for NH_4Cl , NH_4Br and NH_4I are presented graphically in Fig. 4.4.3. ΔT_{str} is positive for NH_4Cl and increases with increase in the concentration nonlinearly. ΔT_{str} for NH_4Br is almost zero up to $w \simeq 3 \times 10^{-2}$ and thereafter become negative. ΔT_{str} for NH_4I is negative throughout the concentration range and ΔT_{str} versus w is parabolic in nature.

Namoto and Endo [14,15] have studied the variation of ultrasonic velocity as a function of temperature in aqueous solutions of NH_4Cl , NH_4Br and NH_4I in the temperature range 55 to 85°C. The authors reported that the velocity peak temperature remains sensibly constant up to 4.5 mole per cent, independent of the kinds of anions for all the ammonium halides and the behaviour for high concentrations beyond 4.5 mole per cent is quite different according to the kinds of halogen ions. The velocity peak temperature (T_p) increases with increasing concentration for NH_4Cl increasing up to 86°C, a behaviour not observed for any of the electrolyte solutions. The velocity peak temperature remaining sensibly constant for ammonium bromide at 74°C and decreasing for ammonium iodide. They stated that the ionic radius is smaller for Cl^- (1.81 Å), largest 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.

In the present work the ultrasonic velocities in aqueous solutions of ammonium halides were determined in the concentration range 0 - 1.4 m with

accuracy of ± 0.003 per cent. Moreover, the velocity measurements were confined to a narrow temperature range on either side of TSVM (i.e. 64 - 80°C) and measurements were made at 2°C intervals leading to an accuracy of $\pm 0.2^\circ\text{C}$ in TSVM determination.

In view of the improved accuracy in fixing TSVM, the present data of TSVM at different concentrations of halides of ammonium may be considered to depict correctly the structural features of these solutions. While ΔT_{obs} is positive at low concentration becoming negative at high concentration for NH_4Cl , ΔT_{obs} is negative throughout the concentration range studied for NH_4Br and NH_4I . ΔT_{str} is observed to be positive increasing with concentration of NH_4Cl in the concentration range studied, ΔT_{str} is constant and almost zero up to $w \simeq 3 \times 10^{-2}$ and thereafter it is slightly negative in the case NH_4Br . For NH_4I , ΔT_{str} is found to be negative throughout the concentration range studied. These observations indicate that in solutions of aqueous NH_4Cl the structure promoting nature of NH_4^+ dominates the structure breaking nature of Cl^- . In aqueous solutions of NH_4Cl , the structural propensities of NH_4^+ and Cl^- are competitively equal and hence we observe almost zero or a very small negative shift. In aqueous solutions of NH_4I the structure breaking nature of I^- over dominates the structure promoting nature of NH_4^+ and hence we observe ΔT_{str} negative and increasing with increase in the concentration of NH_4I . 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 [136, 137].

At any given concentrations ΔT_{str} for $\text{NH}_4\text{Cl} > \text{NH}_4\text{Br} > \text{NH}_4\text{I}$ indicating the structure breaking nature of $\Gamma^- > \text{Br}^- > \text{Cl}^-$. It may be mentioned here that this is the order found for structure breaking nature of these ions from viscosity B-coefficient [126] and activation energy of viscous flow data [127]. The viscosity B-coefficient for Cl^- , Br^- and Γ^- respectively are -0.007, -0.042 and -0.068. The present study depicts the structural features of NH_4^+ , Cl^- , Br^- and Γ^- ions in aqueous solutions of halides of ammonium unambiguously as compared to the studies made by Namoto and Endo [14,15] on these solutions.