Temperature of Maximum Density of Water-Electrolytes: A Review
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Abstract

Additivity rule is found applicable to the Temperature of Maximum Density (TMD) behavior of strong electrolytes. For the first time a systematic attempt was made to divide Despretz constant K_m of an electrolyte into its individual ionic contributions using partial molal expansivity of a proton, E_{H+}^{∞}. The large and positive deviations in ionic K_m of R_4N^+ cations proved their well-known structure strengthening ability, corroborating satisfactorily with their structure promoting nature found from measurements of many thermodynamic properties. Despretz rule was found to obey for some amino acids. TMD Study by 1) acoustical technique, 2) Convective flow technique and 3) under pressure is also studied.

Keywords: TMD, Despretz rule, electrolytes solution, water structure, Hopes apparatus.

Introduction:

Water is known as universally most useful, structurally most complex, and anomalous liquid known to human beings. It plays an important role in life processes and forms an essential constituent of the animal cells & plant tissues. Two lone pairs of electrons on the oxygen atom, causes two bonded hydrogen atoms to give distinctive V-shape with a bond angle of 104.5°. This polarity gives extensive hydrogen bonding between water molecules which is responsible for many anomalous properties of water.

Some important and well-known anomalies of water are remarkably high melting (0°C) and boiling points (100°C). An especially important anomalous property of water is a Temperature of Maximum Density (TMD) at 3.98 °C. Thomas Charles Hope[1] is the first scientist who recorded the TMD of water in 1805 by measuring convection pattern of water in an assembly of cylinder fitted with two thermometers and a metal basin which is known as Hope's apparatus. Existence of the TMD of pure water was confirmed through a series of experiments by Hope, which was based on observing a temperature inversion due to natural convection, rather than bulk changes in the volume of the water.

Comparable substances like NH_3, CH_4, HF and H_2S behave differently than water. Water exhibit characteristic properties of an associated liquid more remarkable than hydrides of elements of VIA group. The melting & boiling points of these hydrides decreases with decreasing molecular weights from H_2Te, H_2Se to H_2S in an orderly manner, however, water has remarkably high values indicating a presence of strong force, known as hydrogen bonding. Due to this, water exists as monomers, dimmers, polymers, cage like clusters and many complex structures but cavities in the structure give rise to a lower density.

Conway[2] defined the concept of structure in liquid waterin a simple way as follows: Water structure making / breaking ability of the solutes can be defined in terms of the effects on the molecular reorientation time (10^{-11}sec), resulting either from rotational or translational diffusion. If the dissolved solute markedly lengthens this period, it is called as structure maker/ promoter. Conversely, if the dissolved solute shortens this period, it is called as structure breaker.

At 3.98^{o}C, water shows a maximum density due to breaking of hydrogen bonded network which allows the loosened water molecules to occupy the voids in the open structure, resulting in the contraction of volume and increase in density. Thus, the TMD is governed by a critical equilibrium between monomers or dimers and hydrogen bonded water molecules. When a solute is dissolved in water, the above equilibrium is disturbed. If a solute enhances hydrogen bonding (e.g. t-BuOH) then TMD increases and if the solute tends to destroy the hydrogen bonding (e.g. most electrolytes) then TMD decreases.

Apparent straight line plot of shift in TMD ($\Delta\theta_{obs}$) versus 'm'is called as Despretz rule[3], eqn (1).

$$\Delta\theta_{obs} = m. K_m \quad \text{or} \quad \Delta\theta_{obs} = x. K_D \quad \quad (1)$$

The constants K_m (^{o}C/mol/Kg)[4-6] or K_D (^{o}C)[7] known as Despretz constant are characteristic of the electrolytes. 'm' and 'x' are the molality and mole fraction of the dissolved solute respectively.

Rosetti[8,9] reviewed the early work on shift in TMD of water by the addition of a solute for few simple salts. A considerable portion of this work is due to Despretz[3]. Most of the earlier work on TMD of aqueous solutions was carried out using density measurement techniques at higher concentration.

Further, Rosetti[8,9] tried to correlate the shift in the TMD of water to the lowering of its freezing point due to addition of the same solute, but he failed to formulate any general rule between these two phenomena, as the lowering of the freezing point is related to the osmotic pressure of the solution and thus depends only on the concentration. However, shift in TMD is characteristic of the solute i.e. its interactions with the H-bonding and concentration of solute.

Wright[10] studied the lowering of TMD of water for some salts. His findings agreed satisfactorily with the Despretz's Law. He further, found that highly ionized salts of organic acids behaved in the normal manner like strong electrolytes and mineral acids. Coppet[4] & Wright[10] measured the shift in TMD only at 2–3 concentrations which were not enough to evaluate Despretz constant reliably. However, the TMD data of later workers for some electrolytes at 6–7 concentrations are reported in the International Critical Tables[11] which was used by Pokale[12] to calculate Despretz constant graphically using least square fit method. He observed that K_m values for simple electrolytes are always negative. Strong influence of valency and size of the ion is also apparent from this data.

Bernal & Fowler[13] demonstrated applicability of additivity principle to the partial molal volumes (V_2^{∞}) of electrolytes at infinite dilution. Wirth[14] divided V_2^{∞} of the electrolytes into their ionic components by assuming $V_{K+}^{\infty} = V_{F-}^{\infty}$, on the consideration that the crystal radii of K^{+} and F^{-} are nearly identical. This additivity of partial molal volume of electrolytes at infinite dilution in water has also adequately demonstrated by several researchers (Bernal & Fowler[13], Horne[15], Millero[16], Scoot[17], Desnoyers et al[18], Couture & Laidler[19]). This additivity rule was found to extend up to moderate concentrations where ion-pairing is not extensive.

Many other electrolytic properties like viscosity B-coefficient, ionic radii, conductance etc. are also found to obey the additivity rule. Kaminsky[20] demonstrated the additivity of viscosity B-coefficients for aqueous solutions of electrolytes at various temperatures. He assumed $B_{K+} = B_{Cl-}$ based on the almost

identical cation and anion transference number for KCl at all temperatures and calculated ionic B-values for several ions which were in good agreement with those reported by other workers.

Applicability of the additivity rule to the TMD behavior of strong electrolytes was observed by Wright[10] using TMD data of Coppet[4], Wada & Miura[7], Rosetti[8,9], Coppet[4], Wada & Miura[7], Rosetti[8,9] also demonstrated the validity of additivity rule to the TMD behavior of some alkali halides using TMD data reported in literature.(ICT[11]).

Lilley & Murphy[5], derived an eqn. (2) expressing $\partial V_2^\infty / \partial T$ in terms of Despretz constant K_m as given below:

$$- \ \partial V_2^\infty / \partial T = K_m / 64.1 \tag{2}$$

Where V_2^∞ denotes the partial molal volume of electrolyte at infinite dilute.

A good agreement is seen between K_m values evaluated from density measurements using eqn. (2) with the K_m values obtained from TMD measurement (Wright[10] & ICT[11]). However, the data used for TMD and density measurements are at high concentration which cannot yield reliable values. Hence, K_m values reported by them needs to be modified using TMD and density measurements at sufficiently low concentrations, where the Debye – Huckel theory for the ion-water interaction will be valid.

Aims & Objectives:

From the literature[3-11] survey, it is seen that most of the TMD measurement of electrolytes was carried out at high concentration and such data are very difficult to interpret due to presence of various types of interactions present. Thermodynamic properties of aqueous solutions of strong electrolytes at low concentrations can well be interpreted using Debye-Huckel theory. Hence, precision TMD measurements of dilute aqueous solutions of strong electrolytes using sophisticated technique would form valuable information to the researchers in this field. Further, from this precision TMD measurement, it is aimed to develop methodology to evaluate accurate Despretz constant and then limiting ionic Despretz constant. The structure making propensity of tetra-salts from other thermodynamic properties is also to be corelated with TMD study which was wrongly interpreted by earlier workers. Applicability of additivity principle to the TMD study has also to be studied like other thermodynamic properties. It is also proposed to study TMD measurements by other techniques.

Limiting K_m of electrolytes at low concentration:

The Despretz rule was conveniently regarded as orderly behavior of electrolytes at high concentration (Nakanishi et al[21], Wada & Umeda[22,23], Franks & Watson[24], Darnel & Greyson[25], Macdonald et al[26]) however, it was found to be inadequate (Kaulgud & Pokale[27]) from experimental and theoretical grounds due to ion-ion, ion-solvent and ion-distant neighbor interactions.

TMD measurements for electrolytes (Wright[10] & ICT[11]) carried out at high concentrations (0.2 m to 7.4 m) which are far away from Debye Huckel region are not expected to yield reliable measure for solute – solvent interactions due to simultaneous presence of solute – solute interactions.

It is well known that the thermodynamic properties of electrolytes in aqueous solution do not obey any linear law, except in very dilute solutions, where the properties are linear functions of the square root of concentration. Particularly, at high concentrations, as are employed in TMD measurements of electrolytes, the thermodynamic properties show strong nonlinear concentration dependence. It is

noteworthy that even the smallest concentration used in most of the TMD measurements by earlier workers are above the Debye – Huckel limiting law.

Disagreement of most of the earlier TMD data with Despretz law becomes clearer from the findings of two slopes i.e. two values of Despretz constant (K_m) for HCl, when Kaulgud & Pokale[27], plotted the earlier TMD measurement data for HCl (0.3 – 3 mol kg^{-1} concentration range). As 0.3 m is not the sufficiently dilute solution, the TMD measurement for less than 0.3 m solutions further, was expected to yield different value of K_m for HCl and other electrolytes also. Similarly, two different slopes i.e. two values of Despretz constant(K_m) for sulphuric acid also were reported (Pokale[12]) in 0.1–0.8 mol.kg^{-1} concentration range. This necessitated developing proper method for the unambiguous evaluation of limiting ionic K_m.

It may be noted that Bottomley et al[28] from a careful study of apparent molal volume verified that the Debye Huckel limiting law is clearly followed for many multivalent electrolytes within the concentration range of 0.001 – 0.01 mol kg^{-1}.

Thus, considering importance of TMD measurements of strong electrolytes in dilute solutions for the conformity of the data to the Debye – Huckel limiting law, Kaulgud & Pokale[27] carried out TMD measurements of alkali & ammonium halides at lower concentration (0.002 – 0.08 mol kg^{-1}) using twisted 'W' type dilatometer in a 60L bath, capable of maintaining temperature within $\pm$ 0.02 $^{\circ}$C, developed earlier by Kaulgud et al[29] to investigate reliable limiting Despretz constant. Kaulgud & Pokale[27] also carried out TMD measurements of dilute aqueous solutions of acids (HCl, HNO$_3$, H$_2$SO$_4$ and HClO$_4$), considering unique position of the H$^+$ ion for many electrolytes in aqueous solutions.

Table 1: Corrected and uncorrected Despretz constant K_m ($^{\circ}$C kg mol^{-1}) for low and high concentration.

Solute	K_m Ref.[27]			K_m Ref. [7,11,22-25]		m (mol kg^{-1})
	Eqn.(1)	Eqn.(4)		Eqn.(1)	Eqn.(4)	
LiF	– 3.81	– 3.81		--	--	--
LiCl	– 4.94	– 4.94		– 6.2	– 5.0	0.24 – 1.20
LiBr	– 5.92	– 5.92		– 7.1	– 6.3	0.12 – 0.48
LiI	– 7.96	– 7.76		– 8.4	– 7.7	0.08 – 0.48
NaF	– 8.65	– 8.65		--	--	--
NaCl	– 9.28	– 9.28		– 13.8	– 12.6	0.17 – 1.29
NaBr	– 10.62	– 10.62		– 14.2	– 13.6	0.10 – 0.30
NaI	– 12.15	– 12.15		– 17.0	– 16.5	0.07 – 0.21
KF	– 8.7	– 8.7		--	--	--
KCl	– 8.64	– 8.64		– 11.4	– 10.7	0.14 – 0.42
KBr	– 9.74	– 9.74		– 12.9	– 12.3	0.09 – 0.35
KI	– 11.43	– 11.43		– 15.5	– 14.9	0.06 – 0.32
NH$_4$F	– 6.2	– 6.2		--	--	--
NH$_4$Cl	– 7.11	– 6.72		– 7.2	– 6.8	0.19 – 0.58
NH$_4$Br	– 8.40	– 8.40		– 10.8	– 10.3	0.08 – 0.33
NH$_4$I	– 9.64	– 9.64		– 11.1	– 10.4	0.18 – 0.41
HCl	– 5.11	– 4.74		– 6.4	– 5.4	0.28 – 0.85
				– 12.2	– 9.8	1.14 – 3.01
H$_2$SO$_4$	– 19.11	– 18.32		– 23.4	– 20.5	0.10 – 0.77

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HNO$_3$	-9.39	-9.19		-12.0	-11.4	$0.16-0.32$
HClO$_4$	-15.90	-15.64	RbCl	-11.8	-11.4	$0.08-0.53$
NaHSO$_3$	-10.80	-10.60	CsCl	-12.0	-11.5	$0.06-0.25$
(CH$_3$)$_4$NBr				-9.7	-9.2	$0.06-0.27$
(C$_2$H$_5$)$_4$NBr				-10.8	-10.3	$0.04-0.29$
(n-C$_3$H$_7$)$_4$NI				-14.8	-13.9	$0.02-0.28$
(n-C$_4$H$_9$)$_4$NCl				-17.0	-16.6	$0.12-0.16$

Wakabayashi & Takaizumi[6] tried to apply the Debye–Huckel theory to TMD data for 1:1 electrolytes by deriving the following eqn.(3) using Redlich-Meyer expression for apparent molal volume ($\phi_v = \phi_v^\infty + S_v.m^{\frac{1}{2}} + b_V.m$).

$$\Delta\theta_{obs} = K_m.m + K_m'.m^{3/2} + K_m''. m^2 \qquad (3)$$

Where, $K_m = -64.1. E^\infty$, $K_m' = -1.074$ is the $\partial S_v/\partial T$ dependent term and $K_m'' = -64.1. \partial b_v/\partial T$

Debye-Huckel theory, as was expected, thus gives a non-linear dependence of $\Delta\theta_{obs}$ as a function of molality. Therefore, for all the earlier TMD work of 1:1 electrolyte, the Debye-Huckel theory does not really support a linear concentration dependence of $\Delta\theta_{obs}$.

Thus, neglect of 2nd and 3rd terms in eqn (3), in calculating K_m of salts as has been done by Lilley & Murphy[5]and Wakabayashi & Takaizumi[6] is therefore not justified.

Kaulgud& Pokale[27]used the eqn (4) for dilute solutions by ignoring 3rd term ($64.1.\partial b_v/\partial T.m^2$) on right hand side of eqn (3) which represents ion – ion interactions as it is negligible at low concentrations.

$$\Delta\theta_{obs}+ 1.074 m^{3/4} = K_m.m \qquad (4)$$

Kaulgud& Pokale[27]carried out TMD measurements at low concentrations (0.002 – 0.08 mol kg^{-1}) and obtainedtrue limiting K_m values of electrolytes as the slope of the linear plots of $\Delta\theta_{obs}+1.074 m^{3/4}$ (i.e. corrected $\Delta\theta_{obs}$) versus molality by a least square fit program (Table 1). The effect of correction term becomes clear by comparing corrected and uncorrected K_m values given in Table 1 for TMD data at various concentration ranges.

From Table 1, it becomes clear that limiting K_m of almost all the electrolytes evaluated from TMD measurements at low concentration (Kaulgud & Pokale[27]) are practically unaffected by the correction (eqn.4). However, K_m values of all the electrolytes evaluated from earlier TMD measurement at moderate concentration are seems to be affected due to correction (eqn.4).

From Table 1, order of the limiting K_m for alkali metals and ammonium halides as F$^-$‹ Cl$^-$‹ Br$^-$‹ I$^-$ seems to be interesting. Alkali cations also exhibit similar sequence as K$^+$ ‹ Na$^+$ ‹ Rb$^+$ ‹ Cs$^+$except sodium which forms a peak. Darnell & Greyson[25] from TMD study inferred the order of structure breaking ability as Li$^+$‹ H$^+$‹ K$^+$≤ Rb$^+$ ≤ Cs$^+$. This is the same sequence as that established by other researchers (Kavanan[30] & Greyson[31]) using other thermodynamic techniques to determine influence of solute on water structure. From Table 1, it seems that the sodium ion does not exhibit orderly behavior. A similar behavior of sodium was also observed by Wakabayashi & Takaizumi[6] in a study of K_m vs. standard partial molal entropy of ions. Like peaking of sodium for K_m values, peaking of sodium for coefficient of limiting partial molal expansibilities (α_2^∞) was noticed by Kuppers[32].

From Table 1, it is notable that limiting K_m of HCl and LiCl evaluated from low concentration data are nearly equal. This corroborates with the fact observed by Darnel & Greyson[25] regarding similar

water structure making ability of H^+ and Li^+. Other thermodynamic properties as reported by Robinson & Stokes[33] also corroborate the above finding of HCl and LiCl. e.g. osmotic and activity coefficients at any given concentration of H^+ and Li^+ are nearly equal, and the hydration numbers (h) at 25^oC are also nearly equal (HCl, $h = 8.0$ and LiCl, $h = 7.1$).

Limiting ionic K_m of electrolytes:

Wakabayashi & Takaizumi[6] attempted to divide Despretz constant for electrolytes into their ionic contributions. Using eqn.(5), they derived eqn.(7) like Lilley & Murphy[5] for apparent molal volume (ϕ_{v2}) of solute and eqn.(6) expressing the molal volume (V_1) of water around 3.98 ^oC as parabolic function of temperature:

$$\phi_{v2} = \frac{1}{m} \left[\frac{1000 + m.M}{d} + \frac{1000}{d*} \right] \qquad (5)$$

$$V_1 = V_1^* [1 + \alpha_1 . (\theta - 3.98)^2] \qquad (6)$$

$$K_m = - 64.1 \ x \ E^\infty \qquad (7)$$

Where, d, m, M is density, molality and molecular weight of solute and d^* is density of pure water.

α_1 is thermal coefficient of expansion of water $= 7.8 \ x \ 10^{-6} / ^oC^2$

V_1^* is molal volume of water at 3.98 ^oC

θ is TMD of solution

E^∞ is the partial molal expansibility at infinite dilution.

According to Kaulgud & Pokale[27], method of obtaining K_m using eqn. (7) from E^∞ values is not a correct procedure as it has assumed that $d\phi_v/dT = d\phi_v^\infty/dT$ and ignoring $\partial S_v/\partial T$ dependent term. This approximation is valid for measurement of apparent molal volume only at sufficiently dilute solution and around 4^oC, which was unavailable for electrolytes in literature.

To evaluate ionic Despretz constant for individual ions, Wakabayashi & Takaizumi[6] selected proton H^+ as reference ion by taking the value of E_{H+}^∞ from eqn.(8) of Millero[16] which was obtained from the volumetric data of many workers (Zana &Yeager[34] and King[35])

$$E_{H+}^\infty = - 0.008 - 3.40 \ x \ 10^{-4} \ t \qquad (8)$$

Where, t is temperature in ^oC.

Wakabayashi & Takaizumi[6] evaluated ionic K_m of several ions using K_m for H^+ ion $= 0.6 ^oC.mol^{-1}Kg$ from TMD data of electrolytes reported in ICT[11]. As TMD data reported in ICT[11] is at remarkably high concentration, it contains contribution of solute – solute interactions, hence these ionic K_m evaluated using TMD data reported in ICT[11] are not reliable and needs to be evaluated using TMD data at sufficiently low concentration (Debye Huckel region).

Wada et al[36] measured TMD of aqueous solutions of 20 complex salts of transition metals. These salts were also found to obey Despretz law and additivity principle. However, they calculated ionic Despretz constant for the various ions by assuming equal Despretz constant for K^+ and Cl^-. It is to be noted that the ionic Despretz constant for K^+ and Cl^- cannot be the same, since ionic size is not only the criteria for TMD but, the type of ionic charge and orientation of water molecules around the ion, which determine the TMD are bound to be different for cations and anions.

Kaulgud& Pokale[27] for the first time attempted systematically to divide Despretz constant K_m of an electrolyte into its individual ionic contributions. V_{H+}^{∞} values at a given temperature calculated by various methods were found to differ, however, the partial molal expansivity of a proton, E_{H+}^{∞} determined by all the methods was found to be a linear function of temperature (eqn.8). This merit of E_{II+}^{∞} was used by Kaulgud & Pokale[27] to compute the limiting ionic Despretz constants of many ions using ionic K_m of $H^+ = + 0.6$ °C kg mol^{-1} (from eqn.8) and corrected K_m (eqn.4) of electrolytes from TMD measurements of dilute solutions (Table 2).

Table 2: Limiting Ionic Despretz constant K_m (^{o}C kg mol^{-1}) .

Catons	K_m Ref. [27]	K_m Ref. [6]	Anions	K_m Ref. [27]	K_m Ref. [6]
H^+	+ 0.60	+ 0.6	F^-	− 4.58	− 7.1
Li^+	+ 0.40	+ 1.5	Cl^-	− 5.34	− 6.5
Na^+	− 3.94	− 6.1	Br^-	− 6.62	− 7.9
K^+	− 3.30	− 4.4	I^-	− 8.19	− 10.4
NH_4^+	− 1.38	+ 0.1	NO_3^-	− 9.79	− 12.5
Rb^+	− 6.0 [11]		ClO_4^-	− 16.22	
Cs^+	− 6.1 [11]		HSO_3^-	− 6.63	
Me_4N^+	− 2.6 [7,24,25]		SO_4^{2-}	− 19.52	
Et_4N^+	− 3.7 [7,24,25]				
$n\text{-}Pr_4N^+$	− 5.7 [7,24,25]				
$n\text{-}Bu_4N^+$	− 11.3 [7,24,25]				

Limiting Ionic K_m and Tammann-Tait-Gibson (TTG) model:

Wakabayashi & Takaizumi[6] tried to correlate K_m with the standard partial molal entropy of ions in water and found two different lines for cations and anions. Millero[37] also found a linear graph by plotting E^{∞} vs. Z^2/r for Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, where 'Z' and 'r' are charge and Pauling ionic radius of the ion respectively. Kaulgud & Pokale[27] tried to correlate K_m with Pauling ionic radii (r) but failed to find any regularity. The reason for this irregularity seems to be the use of Pauling radii which probably do not correspond to the effective size of the ions in water, it is due to the ion-water interactions leading to electrostriction and the change in the structure of water.

It is well known that, size, shape, type, and charge of the dissolved ions play an important role in influencing the structure of water. The resulting complex changes in the volume of water are available in the work of Leyendekkers[38-43] based on the Tammann-Tait-Gibson (TTG) model. TTG model was successfully applied by Leyendekkers to volume, refractive index, heat capacity and transport property like viscosity.

Leyendekkers calculated values of intrinsic volumes of many salts, and this parameter is related to the compressibility and density of the solution and of pure water. Leyendekkers computed effective ionic radii (r + Δ) in aqueous solution at 25°C using reliable density data of aqueous solutions in conjunction with the TTG model. 'Δ' defines positional correlation of the ion and adjacent water molecules or the packing effect.

Due to non-availability of reliable and precise density data of dilute aqueous solution around 4 $^{\circ}$C, Kaulgud & Pokale[27] plotted ionic K_m values around 4 $^{\circ}$C for all the cations and anions studied by them including tetra alkyl ammonium cations, and rubidium and cesium vs. $(r + \Delta)$ computed by Leyendekkers at 25 $^{\circ}$C. From this plot, they noticed a much more orderly behavior of K_m vs. $(r + \Delta)$ showing two nearly parallel straight lines for cations and anions. The limiting ionic K_m value thus seems to be governed by the effective volume of the ions in aqueous solution.

TMD Study of Quaternary Alkyl Ammonium Halides:

Wada & Miura[7], Wada & Umeda[22,23] and Darnell & Greyson[25] studied the effect of several quaternary alkyl ammonium halides on the TMD of water and observed the most surprising results that the quaternary alkyl ammonium ions lowered the TMD of water and the order of the effect increases in the sequence $H_4N^+ < Me_4N^+ < Et_4N^+ < n\text{-}Pr_4N^+ < n\text{-}Bu_4N^+$. Thus, larger the alkyl group, greater is the lowering of TMD i.e. greater is the apparent structure breaking ability. This is particularly noteworthy, since it has been generally agreed, based on room-temperature measurements such as partial molal volume (Conway & Verral[44], Padova & Abrahamer[45], Franks & Smith[46], Desnoyers & Arel[47], Millero & Drost-Hansen[48], Lee & Hyne[49]), transport properties (Kay et al[50], Evans et al[51], Horne & Young[52] heats of dilution (Wood et al[53]), solubilities (Franks & Clarke[54], Worth & Surdo[55]), near infrared spectra (Bunzl[56]), association equilibria (Worth[57], Daneai et al[58]), adiabatic compressibility (Conway & Verral[44]) and theoretical considerations, that the R_4N^+ ions are water structure promoters in aqueous solutions and that their structure – promoting ability increases with the alkyl group size (Kavanan[30]).

It is well known that positive excess expansibilities, $\partial/\partial T$ (V_{mix}^E) of aqueous solutions of electrolytes, results in negative contribution of $\Delta\theta_{str}$ and is associated with their water – structure breaking propensity. Therefore, on this basis, quaternary alkyl ammonium halides may be expected to result large enough positive $\Delta\theta_{str}$ contribution to overcome negative $\Delta\theta_{id}$ contribution so that $\Delta\theta_{obs}$ becomes positive. Furthermore, positive $\Delta\theta_{str}$ contribution should increase with the increase of size of the alkyl group in these salts corresponding to their water – structure strengthening (Sharma et al[59]) propensity.

Thus, effect of these ions on water structure appears to show inversion between room temperature and 4 $^{\circ}$C (i.e. TMD). This finding is abnormal because no such inversion is observed at TMD for the halides and alkali ions in other thermodynamic study. It was observed (Darnell & Greyson[25]) that the structure breaking sequence of the halide ions in the quaternary alkyl ammonium halides was independent of the associated cation. Hence, structure – breaking or strengthening ability cannot be attributed to the influence of counter ions. Darnell & Greyson[25] then concluded that at least in the neighborhood of TMD, ion size plays an important role in influencing water structure than the structure making / breaking ability of the ion at room temperature. This conclusion of Darnell & Greyson[25] seems to be inconsistent with the fact that at lower temperature, the structure making ability of R_4N^+ ions are greater as found in the studies of near - Infra – Red Spectra (Worley & Klotz[60], Klotz[61]) of Bu$_4$NBr, the NMR chemical shifts of the water proton in aqueous solution of R_4NX (Rousselot et al[62], Kreishman & Leifer[63]) and the temperature dependence of cationic partial molal heat capacities of R_4N^+ ions in water (Perron et al[64]). The decrease in water–structure making ability of any alkyl groups with decrease in temperature has never been observed by any method so far.

To evaluate the influence of hydrophobic salts on the water structure, estimation of $\Delta\theta_{str}$ from $\Delta\theta_{obs}$ is needed, which is generally exceedingly difficult because for this, volumetric properties of the salts in a hypothetical pure liquid state are required. Takaizumi & Wakabayashi[65] tried to examine $\Delta\theta_{obs}$,

measured for a series of salts which have nearly the same volumetric properties but have different interactions with water structure. This condition is satisfied comparatively well by quaternary phosphonium salts, $(n\text{-}Bu)_{4-n}Ph_nPX$ (where n = 0 to 4) which were used for TMD study by them. Their standard partial molal volumes tend to approach one another as the temperature is lowered, and the structure making ability decreases with n. Takaizumi & Wakabayashi[65] found nearly linear relationship between $\Delta\theta_{obs}$ and concentrations for the salts studied.

Takaizumi & Wakabayashi[65] further tried to divide Despretz constant K_D into volume dependent term K_v and the structural term K_{str} given by the following eqn. (9)

$$K_D = -(K_v + K_{str}) \qquad (9)$$

For electrolytes containing larger alkyl / organic parts (like R_4N^+) K_v contributes largely to K_D. This eqn (9) is derived from the well-known eqn (10) of Wada & Umeda[22,23] in which structural effects are quantitatively expressed.

$$\Delta\theta_{obs} = \theta - \theta_W = -[x_2\alpha_2 V_2^*/2(1-x_2)\alpha_1 V_1^* + \partial/\partial T(V_{mix}^E)/2(1-x_2)\alpha_1 V_2^*] \qquad (10)$$

$$\text{Or} \qquad \Delta\theta_{obs} = \Delta\theta_{id} + \Delta\theta_{str}$$

This is obtained by equating the temperature derivative of the molar volume of the solution to zero concentration, keeping in mind that the molar volume of water has a parabolic dependence on temperature near TMD.

Where θ and θ_W are the TMDs of solution and pure water; x_2, α_2, V_2^* are the mole fraction, coefficient of cubical expansion and molar volume (at 0^oC) of pure solute and α_1, V_1^* are the expansion coefficient and molar volume of pure water at θ_W (=3.98^oC). V_{mix}^E is the excess volume of mixing. The first term in eqn(10), $\Delta\theta_{id}$ represents the decrease in TMD due to accommodation of the solute in the cavities of suitable size, when the solution behaves ideally (i.e. $V_{mix}^E = 0$).

Takaizumi & Wakabayashi[65] estimated values of K_v & K_{str} for the R_4P^+ ions and found large negative values of K_{str} indicating a strong structure making ability of the cations. But this structure making ability of these cations is over shadowed by still larger K_v values. And hence, the net result is the depression of TMD of water by the salts of R_4P^+ and R_4N^+ ions.

Since, the shift in TMD is a resultant effect of ideal mixing and solute – solvent interactions (Wada & Umeda[22, 23], Franks & Watson[24]) without considering the contribution of ideal mixing, it is impossible to conclude solute – solvent interactions from K_D values alone.

However, change in heat capacities of solute in water directly gives the influence of solutes on water structure (Subramanian & Ahluwalia[66]). This aspect was studied by Sarma & Ahluwalia[67] and they investigated change in partial molal heat capacity in aqueous solution of highly structure making salts especially Bu_4NBr and Pr_4NI etc. from room temperature to TMD (Table 3) to see if the behavior of these salts as structure makers is reversed near TMD as suggested by Wada & Umeda[22, 23], Wada & Miura[7] and Darnell & Greyson[25].

Table 3: ΔC_p^∞ (Cal mol^{-1} deg) reported by Sarma & Ahluwalia[67]

Solute	4 ^{o}C	10 ^{o}C	15 ^{o}C	20 ^{o}C	30 ^{o}C
Bu$_4$NBr	212 $\pm$ 20	186 $\pm$ 7	--	187 $\pm$ 6	179 $\pm$ 3
Pr$_4$NI	121 $\pm$ 4	--	113 $\pm$ 3	--	119 $\pm$ 4

From Table 3, it may be seen that ΔC_p^∞ of aqueous solutions of Bu$_4$NBr and Pr$_4$NI at 4 to 30 ^{o}C are all positive and sufficiently large in magnitude indicating that these solutes are very strong structure makers not only at room temperature but also near TMD as well. Thus, the conclusions of earlier authors probably due to improper interpretation of TMD measurements (Wada & Umeda[22,23], Darnell & Greyson[25], Wada & Miura[7]) are at variance with those drawn by Sarma & Ahluwalia[67] from their ΔC_p^∞ results.

It is to be noted that halides of R$_4$N$^+$ in monohydric alcoholic (MeOH to BuOH) solution have shown negative solvation effects, while the alkali metal halides have exhibited positive solvation effects, indicating the different behavior of tetra-alkyl ammonium halides than corresponding alkali metal halides. It was not possible for the earlier workers to corelate negative K$_m$ values of R$_4$N$^+$ cations with their water structure strengthening ability which is proved by many thermodynamic and transport properties. Based on the above discussion, it is especially important to be careful in interpreting the nature of solute – water interactions from TMD study alone for solutes containing long carbon chain without due attention to their effective volume in aqueous solution.

As mentioned earlier, Kaulgud & Pokale[27] while TMD measurements of simple electrolytes in dilute solution, plotted ionic K$_m$ values vs. (r + Δ) computed by Leyendekkers[38-43] at 25 ^{o}C for all the cations and anions including tetra alkyl ammonium cations (Wada & Miura[7], Franks & Watson[24], Darnell & Greyson[25]). They noticed a much more orderly behavior of limiting ionic K$_m$ vs. (r + Δ) showing two nearly parallel straight lines for cations and anions. By careful examination of this plot, it becomes clear that R$_4$N$^+$ cations lie very much above the straight line of cations. This large and positive deviations in ionic K$_m$ (ΔK$_m$= 18, 23, 27 and 25) observed for Me$_4$N$^+$, Et$_4$N$^+$, n-Pr$_4$N$^+$ and n-Bu$_4$N$^+$ cations respectively are noteworthy and can definitely be regarded as an indication of their water structure strengthening propensity. This large and positive deviations in ionic K$_m$ of R$_4$N$^+$ cations are an unequivocal proof of their well-known structure strengthening ability, which can offset the effect of their volume on water structure, which is generally structure breaking.

TMD Study of Long Chain Carboxylate ions & Amine Hydrochloride ions:

Deshpande[68,69] carried out TMD measurements of aqueous solution of (1) sodium salts of formate, acetate, propionate, butyrate, valerate, caproate and caprylate and (2) hydrochlorides of butylamine, hexylamine and heptylamine to estimate limiting ionic K$_m$ values by using eqn(4) and additivity principle. To interpret the TMD results (Table 4), he plotted limiting ionic K$_m$ of carboxylate anions and alkyl ammonium cations against their radial length, along with the plot of limiting ionic K$_m$ versus effective ionic radii of many cations and anions studied earlier (Kaulgud & Pokale[27]).

Carboxylate anions and alkyl ammonium cations were found to lie on two separate lines far above (positive side) the two lines found earlier (Kaulgud & Pokale[27]) for simple ions, which is reminiscent with the earlier findings for tetra alkyl ammonium cations forming a line on more positive side. K$_m$ being the sum of volumetric and structural components (eqn.9), it can be said that K$_m$ of long

chain cations and anions contains more structural component and less volumetric component. The large positive deviation of limiting ionic K_m for these long chain ions can surely be regarded as an indication of the water structure strengthening propensity.

Classical ions are electro-strictive in nature, which tend to break the structure of water. But the long chain ions due to hydrophobic group stabilizes the water structure, thereby increasing the structural component of K_m, resulting in less negative values of ionic K_m. When long chain molecule interacts with water, reforming of water structure takes place due to hydrophobic group. This tendency increases with the increasing length of hydrophobic group. Formate ion being strongly electrostrictive showed exceptional behavior with more negative K_m than expected.

It is noteworthy from the graph (Deshpande[68, 69]) of ionic K_m versus radial length for carboxylate anions and alkyl ammonium cations that the line for RCOO⁻ions falls below the line for R_4N^+ ions. This was ascribed to the fact that weaker structure stabilization is provided by the hydrophobic RCOO⁻ions compared to corresponding R_4N^+ ions.

It has been agreed that the carboxylate ions are structure makers and their structure promoting ability goes on increasing with increasing chain length, based on the studies of Compressibility & apparent molal volume (Kaulgud & Rao[71]), entropies of ionization (Kaulgud & Pandya[73]), enthalpies of dilution (Seigfried[74]), Infra-red spectra (Hartman[75]), activity & osmotic coefficients (Diamond[76]), specific heat capacities (Ahluwalia & Chawala[77]). Similar increase in structural promotion with increase in size of alkyl group was reported for R_4N^+ ions (Wada & Umeda[78]). Thus, TMD studies of long chain ions like RCOO⁻ions without considering the volume of ions cannot explain their structure making ability.

Table 4: Radial length[70], limiting ionic[68,69] K_m, Compressibility[71] (ϕ_k^∞) & apparent molal volume[16] (ϕ_v^∞)

Ion	Radial length (A°)	K_m (K.Kg.mol⁻¹)	(ϕ_k^∞)x10¹⁰ cc.dyne⁻¹.mol⁻¹	(ϕ_v^∞)ml.mol⁻¹
HCOO⁻	2.325	− 9.22	− 14.3	24.60
CH₃COO⁻	3.855	− 5.70	− 33.0	38.75
C₂H₅COO⁻	5.385	− 9.26	− 53.9	52.82
C₃H₇COO⁻	6.915	− 11.35	− 56.3	68.41
C₄H₉COO⁻	8.445	− 11.70	− 60.2	
C₅H₁₁COO⁻	9.975	− 14.32	− 62.7	
C₆H₁₃COO⁻	13.035	− 21.64		
CH₃NH₃⁺	3.582	− 2.54[72]	− 15.21	36.11
C₂H₅NH₃⁺	5.112	− 4.02[72]	− 18.89	52.94
C₃H₇NH₃⁺	6.642	− 3.43[72]	− 36.72	69.44
C₄H₉NH₃⁺	8.172	− 5.63	− 54.09	85.50
C₆H₁₃NH₃⁺	11.232	− 6.59	--	117.33
C₇H₁₇NH₃⁺	12.762	− 11.70	--	133.23

Sodium carboxylate was interpreted as structure breaker from the study of concentration variation of apparent molal volumes (Watson & Felsing[79]). However, they could not explain the hydrophobic structure making properties of sodium carboxylate as confirmed from excess enthalpies and entropies. Similar controversy has been observed for other solutes also. It is suggested that the classification of solutes as structure makers/breakers is frequently ambiguous and dependent on the physical property under examination.

It appears that negative limiting ionic K_m values are in general less negative for RNH_3^+ ions (Table 4) as compared to that of R_4N^+ ions (Table 2) for similar alkyl group. This means RNH_3^+ ions are more structure stabilizer as compared to corresponding R_4N^+ ions. This difference becomes more for larger alkyl group as in case of butyl group. Similar findings were reported during viscosity B–coefficient ($B_{\eta str}$) and Compressibility (ϕ_k^∞) studies (Kaulgud et al[80]) of $MeNH_3^+$, $Me_2NH_2^+$ and Me_3NH^+ ions which indicate that n–alkyl substituted ions destabilize the water structure in the increasing order of substitution. All these findings imply that the shift in TMD, particularly due to long chain ions is a complex function of i) charge ii) size & shape and iii) effective ionic radii or radial length.

TMD Study of Ionis liquid solutes:

Tariq et al[81], carried out for the first time TMD measurements of aqueous ionic liquid solutes. From the high precision volumetric data on aqueous solutions of different types of ionic liquids they analysed the TMD shifts for sets of ionic solutes and explained the overall effects in terms of hydrophobic, electrostatic and hydrogen-bonding contributions. They discussed the observed TMD shifts and salting-in or salting-out effects produced by the same type of ions considering the different types of possible solute–water interactions. They also claimed some insights concerning the nature of the ions that constitute typical ionic liquid solutes. They reported consistency of their findings with previous results establishing hydrophobic and hydrophilic scales for ionic liquid ions due to their interactions with water.

TMD Study of Amino acids:

Thirumran & Inbam[82] carried out thermodynamic and transport Studies on some basic amino acids in aqueous sodium acetate solution at different temperatures. Due to presence of two functional groups viz. basic amino (-NH₂) and a carboxylic acid (-COOH) group, amino acids in aqueous solution forms 'Zwitterion' by transfer of H^+ ion of -COOH group from one end of the amino acid molecule to its other end of -NH₂ group. The Zwitterion as a whole is electrically neutral; however, it contains negative charge at one end and another end is positive. They[82] carried out ultrasonic, density and viscosity measurements on L-arginine, L-lysine and l-histidine in aqueous sodium acetate solution (0.4mol.kg⁻¹). These amino acids are hydrophilic as they contain polar R– groups and forms hydrogen bonding with water molecules. From the study of some amino acids, they found the molecular association in the order of L-arginine, L-lysine and l-histidine.

Diego et al[83] studied temperature of maximum density for binary aqueous solutions of five amino acids viz. l-tyrosine, l-tryptophan, l-histidine, l-phenylal anine, and l-proline and found the lowering of TMD for all these compounds obeying Despretz rule. Despretz constants calculated by them were found between -9.85 $K \cdot mol^{-1} \cdot kg$ for proline and-16.6 $K \cdot mol^{-1} \cdot kg$ for tyrosine. They found a thermodynamic consistency between partial molar volume calculated from density measurements and TMD results.

TMD Study by acoustical technique:

Foster & Finch[84] used acoustical technique for measuring the temperature of maximum density of dilute aqueous solutions, in which sound transients generated by pulses of microwave energy in aqueous solutions was used to measure TMD rapidly and accurately. Amplitude of these sound transients being proportional to thermal expansion coefficient of aqueous solution 'α' and thus vanishes at TMD. They verified this method by measuring TMD of distilled water and dilute aqueous solutions of sodium chloride.

TMD Study by Convective flow technique:

Cawley et al[85] described a technique for direct determination of the TMD of water solutions using a convective flow technique as a function of concentration and reported to be accurate method. In this method, an anomalous feature is detected in a series of temperature sensor profiles when the liquid sample is slowly cooled through the region of maximum density. Using computational fluid dynamics (CFD), TMD results were presented for a variety of aqueous solutions (ionic salts, sugars, ketones, and alcohols) by assuming a conservative error of ±0.2 ^{o}C applicable to all their TMD measurements. However, this error is very high compared to temperature accuracy (+ 0.002 ^{o}C) reported in the TMD assembly developed earlier (Kaulgud et al[29]). Moreover, they preferred higher concentration range to carry out TMD measurements of electrolytes viz. NaCl (0.4 moles ltr^{-1}), KBr (0.3 moles ltr^{-1}), KI (0.24 moles ltr^{-1}), and much higher concentration (2.2 moles ltr^{-1}) for some non-electrolytes. They compared their findings of linear relationship of shift in TMD versus concentration and reported to be in good agreement with the data of International Critical Tables[11], which was also measured at higher concentration. As already pointed out all these high concentration data are beyond Debye Huckel range and Despretz law is inadequate to accommodate these data, hence, such TMD measurements are unable to give reliable measures as illustrated in eqn.(4).

TMD Study under Pressure:

Due to the importance of equation of state for Sea water, various researchers have investigated physical properties of seawater and pure water as a function of pressure. Gerard Cotter[86] carried out study of the change in the temperature of maximum density of water and aqueous solutions as a function of pressure by direct measurement of thermal expansion of seawater under pressure.

For measurement of TMD, Bradshaw & Schleicher[87]measured the thermal expansion of seawater using dilatometer under pressure. Using a high-pressure magnetic float densimeter, Chen and Millero[88], studied the specific volume of seawater at high pressure. Further, Chen et al[89] and Chen & Millero[90] studied the seawater equation of state by measuring velocity of sound. High pressure equation of state for seawater was modified by Millero et al[91] using data of all these workers. Henderson & Speedy[92] measured the TMD using a fine helical capillary and the Berthelot tube principle at negative pressures.

From the graph of density versus temperature at different applied pressures drawn using the seawater state equation of Fofonoff & Millard[93], Gerard Cotter[86] observed that the TMD of pure water decreases with increasing pressure at a rate of –0.02051 °C/bar which is approximately 1 °C per 50 bar. He also noted more lowering of TMD under pressure for saline water than the pure water.

For the solution with a salinity of 10 practical salinity units, rate of change of the TMD with respect to pressure, was noted to be–0.02101 °C/bar (Gerard Cotter[86]) further, this rate of change of the TMD was found to be steeper as compared to that of pure water as the salinity is increased.

Gerard Cotter[86] studied the TMD of aqueous solutions of three groups of solutes i) sodium chloride, potassium bromide, ii) ethanol, 1-propanol, 2-propanol and iii) sucrose, glucose and acetone as a function of pressure (range 0 to 100 bar) and concentration and the rate of change of the TMD was calculated. He found decrease in TMD by applying pressure to a solution and the rate of change in TMD was found to depend on the solute and its concentration. He also found that the three groups of solutes behaved very differently.

Discussion:

Additivity rule valid for other thermodynamic properties like partial molal volumes (V_2^{∞}), viscosity B-coefficient, ionic radii, conductance etc for aqueous solutions of electrolytes is also found applicable to the TMD behavior of aqueous solutions of strong electrolytes at low concentrations where Debye Huckel theory is valid. Apparent straight-line behavior of shift in TMD ($\Delta\theta_{obs}$) versus concentration is called as Despretz rule. This rule was conveniently regarded as orderly behavior of electrolytes at high concentration; however, it was found to be inadequate by Kaulgud from experimental and theoretical grounds due to ion-ion, ion-solvent and ion-distant neighbor interactions. Further, true limiting K_m values of electrolytes were evaluated as the slope of the linear plots of $\Delta\theta_{obs}+1.074\ m^{3/4}$ (i.e. corrected $\Delta\theta_{obs}$) versus molality by a least square fit program. For the first time a systematic attempt was made to divide Despretz constant K_m of an electrolyte into its individual ionic contributions using partial molal expansivity of a proton, E_{H+}^{∞}.

The large and positive deviations in ionic K_m of R_4N^+ cations proved their well-known structure strengthening ability, corroborating satisfactorily with their structure promoting nature found from measurements of many thermodynamic properties. Similarly, large positive deviation of limiting ionic K_m for long chain carboxylate anions and alkyl ammonium cations is regarded as an indication of their water structure strengthening propensity.

Despretz rule was found to obey for some amino acids viz. l-tyrosine, l-tryptophan, l-histidine, l-phenylalanine, and l-proline from their TMD measurements.

Conclusion:

Additivity rule is valid for Temperature of Maximum Density (TMD) of strong electrolytes. Despretz rule for electrolytes at high concentration is inadequate from experimental and theoretical grounds due to ion-ion, ion-solvent, and ion-distant neighbor interactions. Reliable individual ionic Despretz constant K_m of electrolytes has been evaluated using partial molal expansivity of a proton, E_{H+}^{∞}.

No regular relationship was found between K_m with Pauling ionic radii (r) as probably later do not correspond to effective size of the ions in water due to ion-water interactions leading to electrostriction and the change in the structure of water. A much more orderly behavior of K_m versus effective ionic radii (r + Δ) for all the cations and anions including tetra alkyl ammonium cations is remarkable showing two nearly parallel straight lines for cations and anions. The limiting ionic K_m values thus seem to be governed by the effective volume of the ions in aqueous solution.

Measurement of TMD of aqueous solution using twisted W-type dilatometer wherein volume of solution in capillary is measured by travelling microscope seems to be precision technique, however, this technique is more time consuming. The methods 1) acoustical technique, 2) Convective flow technique and 3) under pressure techniques seems to be less accurate even though they are comparatively fast.

Conflict of Interest:

The authors declare that they have no conflict of interest.

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