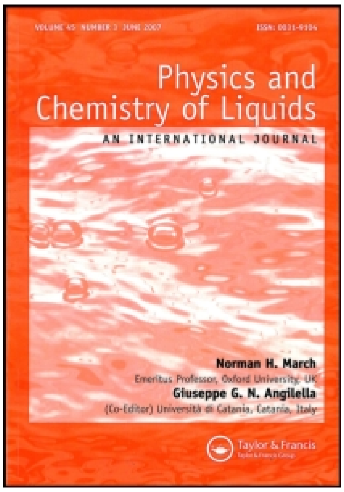

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Determination of Despretz Constants of Some Salts and Ions [1]

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DETERMINATION OF DESPRETZ CONSTANTS OF SOME SALTS AND IONS [1]

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The effect of Me_4NI, n-Bu_4NI, n-$BuEt_3NI$, Et_3PhNI and Et_4NBez on the temperature of maximum density of water was determined using a dilatometric technique. The concentration range was from 0.005 m to 0.050 m in all cases. The temperature data was used to calculate Despretz constants using the equations $\Delta\theta = \theta_{sol} - \theta_w$ and $\Delta\theta = K_m$m, where $\theta_{sol} - \theta_w$ is the difference between temperature of maximum density of the solution and of water, K_m is the Despretz constant. The equation of Kaulgud and Pokale $\Delta\theta + 1{,}074\ m^{3/2} = K_m m$ was also used.

All the calculated K_m's are negative, that is to say, the effect of the salts is to lower the temperature of maximum density. The individual ion constants were calculated using literature values for the iodide and the tetraethyl ammonium ions. The order followed by the absolute values of the constants is $Me_4N^+ < n\text{-}BuEt_3N^+ < Et_3PhN^+ < Bu_4N^+$. The results confirm the proposal of Kaulgud and Pokale in the sense of having the quaternary ammonium ions conserving their influence on the structure of water for temperatures in the neighborhood of that of maximum density of water.

Keywords: Water; maximum density; quaternary ammonium salts; Despretz constants

1. INTRODUCTION

The effect of dissolved substances on the temperature of maximum density of water, θ has been the subject of several studies over the years (see i.e. 2–7). In particular, the effect of water structure makers and breakers have called the attention of several authors [3, 6]. The experimental data have been explained in a variety of ways, some of them in contradiction with the others. Recently Kaulgud and Pokale [7] offered explanations that rationalize the behavior of tetraalkyl ammonium ions with respect to θ. In this work we report Despretz constants for Me_4NI, n-Bu_4NI, n-$BuEt_3NI$, Et_3PhNI and $Et_4NBez^{(Benzoate)}$ in the concentration range from 0.005 m to 0.050 m. Our results are in good agreement with those of reference [7].

2. EXPERIMENTAL

The substances employed were potasium chloride and sucrose Merck R. A., tetrabutyl ammonium iodide and tetramethyl ammonium iodide from Sigma Co., triethyl phenyl ammonium iodide and tetraethyl ammonium benzoate from Eastman Kodak Co. The *n*-butyltriethyl ammonium iodide was sintetized in this laboratory. All salts were purified and annalized following procedures from the literature and adapted in the laboratory [8]. The purity, determined by anion content was 99.9 % for all the salts except for the benzoate whose purity from cation content was 95.7 %. The water used was purified according to recommended procedures [9]. All solutions were prepared by weight using a Mettler AT 261 balance.

The dilatometers used were built following the design of Wright [10]. The experimental set-up is shown in Figure 1. Temperature was controlled by means of a Bayley 123 unit which allows maximum deviations of about ±0.002°C. Heights were measured with a Gaertner Sci. Co. cathetometer readable to ±0.001 cm. Beckmann differential thermometers 5°C full scale, were used for temperature measurement. The Beckmann thermometers were chequed against a NITS certified conventional thermometer.

In a typical run, the dilatometers filled with water or solution were cooled to 12°C and maintained at that temperature for at least one hour. The height of the liquid in the capillary was recorded and observed for an additional half hour to make sure that the volume remained constant. The temperature was slowly lowered to about 6°C. Beginning at this point, height was read at fixed temperatures separated 0.1 to 0.3°C. Each temperature was kept constant for at least one hour. Readings at 10 minute intervals are made until height was constant to ±0.001 cm.

The minimum height was determined for water and KCl solutions to calibrate the method. The calibration was chequed against the data of

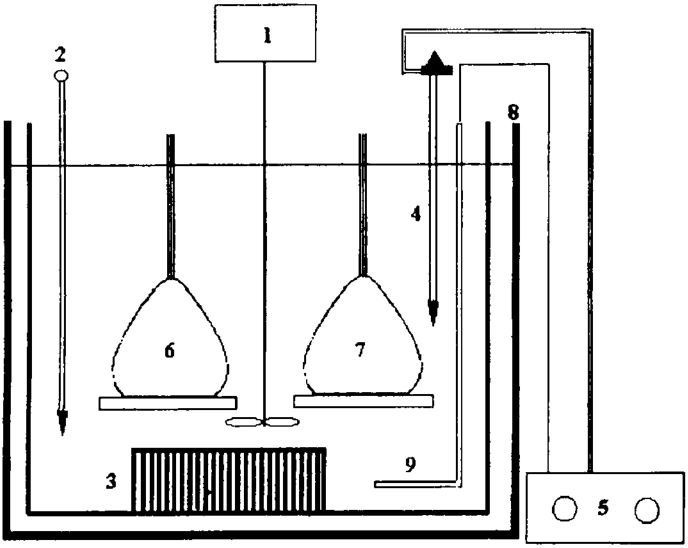

FIGURE 1 Experimental set-up. 1. Stirrer; 2. Beckmann diferential Thermometer; 3. Cooling coil; 4. Temperature sensor; 5. Temperature control; 6. Dilatometer 1; 7. Dilatometer 2; 8. Isolating wall; 9. Heating element.

Garrod and Herrington [2] for sucrose. The results showed good agreement as it can be seen in Table I.

3. RESULTS AND DISCUSSION

The experimental data were used to determine the temperature of minimum height for each of the solutions. The calibration runs provided empirical equations to correct the raw data. The estimated accuracy of the corrected values is 0.01°C. Tables II, III and Figure 2, show the data for the salts studied and the calculated constants using the equations:

$$\Delta\theta_{obs} = \theta_s - \theta_w \qquad (1)$$

and

$$\Delta\theta_{obs} = K_m \text{ m} \qquad (2)$$

TABLE I Variation of θ (°C) with molal concentration for the system Sucrose-Water

m (mol Kg^{-1})	θ (°C)^a	m(mol Kg^{-1})	θ (°C)^b	θ (°C)^c
0.00000	3.98	0.00000	3.958	3.958
0.00759	3.84	0.00760	3.838	3.888
0.01296	3.70	0.01296	3.758	3.768
0.03464	3.46	0.03461	3.398	3.418
0.04965	3.16	0.04965	3.158	3.168
0.06465	2.92	0.06465	2.898	2.898

(a) Data using reference 2.
(b) Data using dilatometer 1.
(c) Data using dilatometer 2.

It is seen that in all cases $\Delta\theta_{obs}$ is negative as it has been found by other authors. Kaulgud and Pokale [7] propose the equation:

$$\Delta\theta_{obs} + 1.074m^{3/2} = K_m \mathrm{m} \tag{3}$$

for a better analysis of the experimental data. They arrive to this result using the work of Wakabayashi and Takaizumi [5]. The Despretz constants obtained with this treatment are shown in Table III and the corresponding plots in Figure 3. The corrected values differ slightly as shown in Table IV.

Individual ion contributions to Despretz constants have been calculated in reference [5]. This treatment allows interpretation of experimental results in a clearer way. Their values for some ions, including some of those studied in this work are presented in Table V. They are used to calculate Despretz constants for several salts and to compare values from references [5, 7]. This gives an idea of both experimental precision and of validity of the treatment. Table VI shows these results. Table VII contains the Despretz constants for the individual ions of the salts studied in this work, calculated with data from reference [7]. For comparison purposes, the constants were calculated for Me_4NI and n-Bu_4NI and their values are presented in Table VIII.

The work of Darnell and Greyson [6] showed that the effect of the tetraalkyl ammonium salts had the order : $Me_4N^+ < Et_4N^+ < Pr_4N^+ < n\text{-}Bu_4N^+ < n\text{-}Am_4N^+$, this is increasing with number of carbon atoms in the cation. Our results are ordered as follows

TABLE II Variation of $\Delta\ \theta$ with molal concentration of Me_4NI, Bu_4NI, *n*-$BuEt_3NI$, Et_3Ph NI, Et_4NBez-water

n-BuEt₃NI		*Et₃Ph NI*		*Bu₄NI*		*Me₄NI*		*Et₄NBez*	
m(mol Kg^{-1})	$\Delta\theta$(°C)	m (mol Kg^{-1})	$\Delta\theta$(° C)	m (mol Kg^{-1})	$\Delta\theta$(° C)	m (mol Kg^{-1})	$\Delta\theta$(° C)	m (mol Kg^{-1})	$\Delta\theta$(° C)
0.00000	0.00	0.00000	0.00	0.00000	0.00	0.00000	0.00	0.00000	0.00
0.00500	−0.09	0.00490	−0.16	0.00500	−0.13	0.00500	−0.08	0.00500	−0.14
0.01000	−0.17	0.01000	−0.19	0.01010	−0.23	0.01000	−0.16	0.01000	−0.16
0.02479	−0.40	0.02500	−0.46	0.02500	−0.58	0.02500	−0.36	0.02500	−0.35
0.05000	−0.73	0.05000	−0.89	0.04999	−1.12	0.05000	−0.63	0.05000	−0.75

TABLE III Variation of $\Delta\theta + 1.074m^{3/2}$ with molal concentration of Me_4NI, Bu_4NI, *n*-$BuEt_3NI$, Et_3Ph NI, Et_4NBez-water

n-BuEt₃NI		*Et₃Ph NI*		*Bu₄NI*		*Me₄NI*		*Et₄NBez*	
m (mol Kg^{-1})	$\Delta\theta + 1.074m^{3/2}$	m (mol Kg^{-1})	$\Delta\theta + 1.074m^{3/2}$	m (mol Kg^{-1})	$\Delta\theta + 1.074m^{3/2}$	m (mol Kg^{-1})	$\Delta\theta + 1.074m^{3/2}$	m (mol Kg^{-1})	$\Delta\theta + 1.074m^{3/2}$
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0049	−0.0932	0.0049	−0.1563	0.0050	−0.1280	0.0050	−0.0759	0.0050	−0.1396
0.0100	−0.1667	0.0100	−0.1864	0.0101	−0.2268	0.0100	−0.1541	0.0100	−0.1589
0.0250	−0.3955	0.0250	−0.4557	0.0250	−0.5764	0.0250	−0.3520	0.0250	−0.3458
0.0500	−0.7208	0.0500	−0.8753	0.0500	−1.1047	0.0500	−0.6131	0.0500	−0.7380

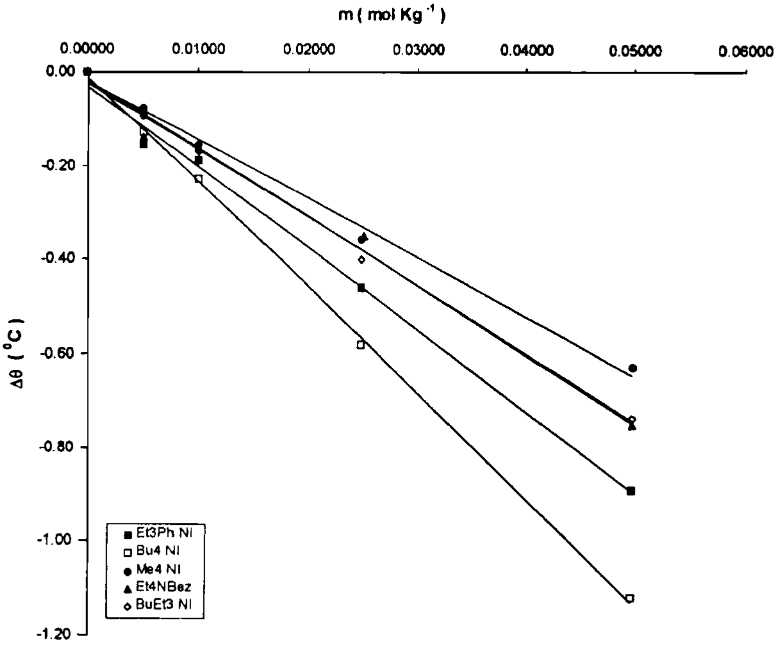

FIGURE 2 Variation of $\Delta\theta$ with molal concentration of Me_4NI, Bu_4NI, *n*-$BuEt_3NI$, Et_3Ph NI, Et_4NBez-Water.

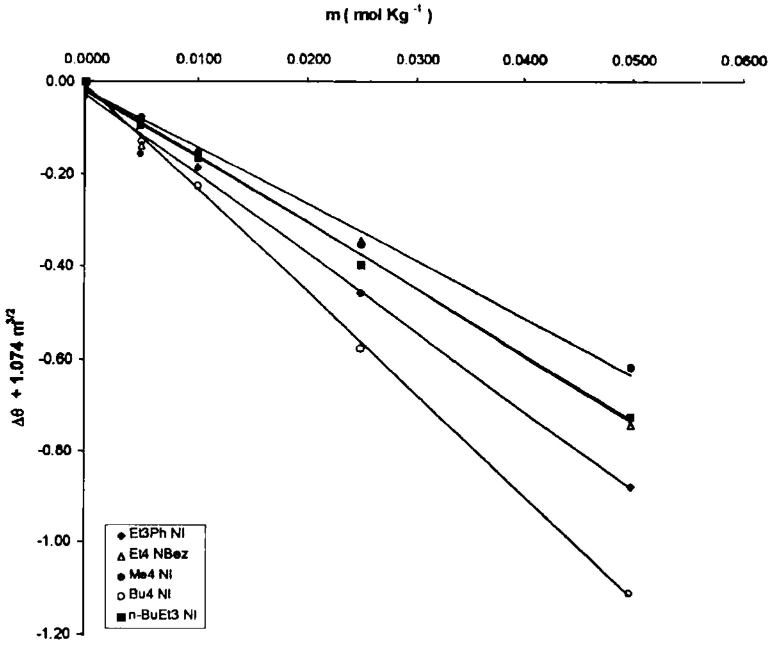

FIGURE 3 Variation of $\Delta\theta + 1.074\ m^{3/2}$ with molal concentration of Me_4NI, Bu_4NI, *n*-$BuEt_3NI$, Et_3Ph NI, Et_4NBez-Water.

TABLE IV Despretz Constants (K_m)

	Me_4NI	*Et_4NBez*	*n-$BuEt_3NI$*	*Et_3PhNI*	*Bu_4NI*
K_m^a	-12.44	-14.32	-14.54	-17.24	-22.28
K_m^b	-12.19	-14.08	-14.28	-16.96	-22.04

(a) From equation $\Delta\theta = K_m m$
(b) From $\Delta\theta = 1.074\ m^{3/2} K_m m$.

TABLE V K_m values for individual ions

Ion	*$K_m (K\ mol^{-1} Kg)$*		
	(a)	(b)	(c)
H^+	0.6		
Li^+	1.5		
Na^+	-6.1		
K+	-4.4		
F^-	-7.1		
Cl^-	-6.5		
Br^-	-7.9		
I^-	-10.4		
NH_4^+	0.0	0.1	
Me_4N^+	-2.0	-1.8	-0.8
Et_4N^+	-3.1	-2.6	-2.6
Pr_4N^+	-3.7		-3.8
Bu_4N^+	-8.0	-9.0	-6.5

(a) Data from Darnell and Greyson
(b) Data from Wada and Miura
(c) Data from Conway and Laliberté.

$Me_4N^+ < n\text{-}BuEt_3N^+ < Et_3PhN^+ < Bu_4N^+$, confirming the above tendency. The effect of aromatic groups in the ions as illustrated by the benzoate anion and by the cation Et_3PhN^+ is comparable to that found by Wakabayashi and Takaizumi [5] for the series Bu_4P^+, Bu_3PhP^+, $Bu_2Ph_2P^+$, $BuPh_3P^+$, Ph_4P^+. This influence is being studied further on in this laboratory using other cations.

The effect of quaternary ammonium cations according to the earliest prediction [6] should be to rise temperature of maximum density of water, this is to give positive $\Delta\theta$ since they are believed to be water structure makers. The maximum in density is supposed to arise from the opposing tendencies of density increase due to structure breaking and density decrease due to thermal expansion. If a solute tends to

TABLE VI Calculated values of K_m from the ionic contributions

			Despretz Constant K_m *(°C mol^{-1} Kg)*	
Solute	K_m^a	K_m^b	Limiting ionic K_m values [c]	Limiting ionic K_m values [d]
$(CH_3)_4NBr$	−9.7	−9.2	(−2.6) + (−6.62) = −9.22	(−2.6) + (−7.9) = −10.5
$(C_2H_5)_4NBr$	−10.8	−10.3	(−3.7) + (6.62) = 10.32	(−3.7) + (7.9) = 11.6
$(n\text{-}C_3H_7)_4NI$	−14.8	−13.9	(−5.7) + (8.19) = −13.89	(5.7) + (−10.4) = −16.1
$(n\text{-}C_4H_9)_4NCl$	−17.0	−16.6	(−11.3) + (−5.34) = −16.64	(−11.3) + (−6.5) = −17.8
$(CH_3)_4NI$	·		(2.6) + (8.19) = −10.79	(−2.6) + (−10.4) = 13.0
$(n\text{-}C_4H_9)_4NI$	–	–	(−11.3) + (−8.19) = −19.49	(−11.3) + (−10.4) = −21.7

(a) Uncorrected values from $\Delta\theta = K_m\, m$

(b) Corrected values using $\Delta\theta - 1.074\, m^{3/2} K_m\, m$

(c) Calculated from ionic contributions data of Kaulgud and Pokale

(d) Calculated from ionic contributions using data of Wakabayashi and Takaizumi for the anions.

TABLE VII Despretz Constants K_m(°C mol^{-1}Kg) for individual ions

Ion	Me_4N^+	$n\text{-}BuEt_3N^+$	Et_3PhN^+	Bu_4N^+	$Benz^-$
K_m	−4.00	−6.09	−8.77	−13.85	−10.38

TABLE VIII Despretz Constants for Me_4NI and *n* - Bu_4NI

Solute	K_m^a(°C mol^{-1}Kg)	K_m^b(°C mol^{-1}Kg)	K_m^c(°C mol^{-1}Kg)
Me_4NI	−12.19	−10.79	−13.00
n-Bu_4NI	−22.04	−19.49	−21.70

(a) This work
(b) Column (c) table VI.
(c) Column (d) table VI.

form structure, its effect on θ should be to rise it. The experimental evidence shows the opposite effect as found by Darnell and Greyson [6]. They propose that at low temperatures, i.e., those near the temperature of maximum density, the structural effect changes sign. This is in disagreement with experimental evidence from other properties [7]. Kaulgud and Pokale offer a different explanation, based in work done by Leyendekkers [11 − 16] they get the effective ionic radii and plot the limiting ionic Despretz constants as a function of these radii. They find a linear behavior for most anions and cations, showing that K_m depends on the effective volume of the ions in solution. The experimental results for the R_4N^+ ions clearly deviate from all the ions in solution. The experimental results for the R_4N^+ ions clearly deviate from all others, showing smaller absolute values for K_m than expected from their effective radii. This is explained as due to the water structure enhancement caused by these ions. Our results for the cations studied give values that are of the same order of those analyzed by Kaulgud and Pokale, conforming their conclusions. The effective ionic radii could not be calculated for the salts here reported because the experimental data necessary is not available at this moment.

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