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The effect of Me_4NBr, Et_4NBr, Bu_4NBr, and $(EtOH)_3EtNBr$ on the Temperature of Maximum Density of Water

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Abstract The densities of aqueous solutions of Me_4NBr, Et_4NBr, Bu_4NBr, and $Et(OH)_3EtNBr$ were measured in the concentration range 0.002 to 0.05 $mol\cdot kg^{-1}$. The temperature of the determinations ranged from 275.15 to 279.15 K in 0.5 K steps, and the uncertainty of the densities was around $\pm 1 \times 10^{-6}$ $g\cdot cm^{-3}$. Eleven concentrations were used for each of the salts.

It was found that all the solutes follow Despretz' law. The absolute value of the Despretz's constants increases with increasing number of carbon atoms in the cation, except for $Et(OH)_3EtNBr$ which has the highest value. The ionic contributions to the Despretz's constants were calculated.

The volumetric data obtained allows the calculation proposed by Kalgud and Pokale. The effective ionic radii were calculated using a semi-empirical equation, as proposed previously by several workers. The nonlinearity of the plot of the ionic Despretz constants versus effective ionic radius is confirmed.

Keywords Water · Tetraalkylammonium salts · Maximum density

1 Introduction

The existence of a temperature of maximum density for water is one of the so-called "anomalies" that make the substance unique in nature [1, 2]. The effect of dissolved substances on this property has received attention since the nineteen century when the French physicist

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Despretz [3] studied it. Since then, there have been a number of studies by several workers, some of the more recent ones being from this laboratory [4, 5].

The experimental technique most frequently used for the measurements is dilatometry [4, 6]. In this work we made direct measurements of density as a function of temperature. For this purpose, a version of a magnetic float densimeter was built, following the design of Vargas and Blanco [7].

2 Experimental Section

A description of the technique and equipment has been reported elsewhere [5, 7].

Water was purified according to recommendations in the literature [8]. The conductivity of the purified water was always less than 4 µS. The KCl used for calibration purposes was Merck analytical grade with purity 99.99%. It was dried at 373 K for 12 h and kept in a desiccator until used.

The symmetric tetraalkylammonium bromides used were obtained as follows: Me_4NBr, Merck, purity $> 99\%$; Et_4NBr, ICN Pharmaceuticals Inc. purity $> 98\%$; and Bu_4NBr, Sigma purity $> 99\%$. They were further purified according to recommendations in the literature [9, 10]. The salts were crystallized from ethanol solutions. Full precipitation was achieved using diethyl ether. After this, they were kept under vacuum until used.

The salt $(EtOH)_3EtNBr$ was prepared according to the method of Wen and Saito [10]. A mixture of triethanolamine in excess and ethylbromide was heated in anhydrous methanol under reflux for 24 h. The resulting salt was purified by repeated crystallizations from ethanol and ethanol + chloroform mixture; it was subsequently kept dry under vacuum.

All the bromides were analyzed after purification and before use for their halide content, by potentiometric titration with $AgNO_3$. The purities were better than 99.9% in all cases.

The solutions were prepared by weight using a Mettler AT 261 balance, which had a sensitivity of $\pm 1 \times 10^{-5}$ g between 0 and 50 g, and of $\pm 1 \times 10^{-4}$ g between 50 and 210 g. The concentration range was varied from 0.00200 to 0.05000 $\text{mol}\cdot\text{kg}^{-1}$.

The densimeter was calibrated [7] using platinum rings and checked using solutions of known density [11]. This procedure is fully described by Torres [5]. The temperature was kept constant to within 0.001 K and densities were measured to $\pm 1 \times 10^{-6}$ $\text{g}\cdot\text{cm}^{-3}$ in the range of temperature from 275.15 to 279.15 K. Measurements were done at intervals of 0.5 K.

3 Results and Discussion

Tables 1 to 4 show the density data obtained for the four salts at the selected temperatures. The data were fitted by equations using the least-squares method, and from them the temperatures of maxima density were calculated.

According to the traditional treatment, Despretz's law is written as:

$$\Delta\theta_{\text{obs}} = K_m m \tag{1}$$

where $\Delta_{\text{obs}} = \theta - \theta_w$. θ and θ_w are the temperatures of maximum density of the solution and of water, K_m is Despretz's constant and m the concentration of the solutions in molality units.

Table 1 Density of aqueous Me_4NBr as a function of concentration and temperature

Temperature (K)	m (mol·kg^{-1})										
	0.00200	0.00500	0.01000	0.01500	0.02000	0.02500	0.03000	0.03500	0.04000	0.04500	0.05000
	Density (g·cm^{-3})										
279.0	1.000020	1.000150	1.000364	1.000566	1.000774	1.000980	1.001185	1.001391	1.001600	1.001803	1.002005
278.5	1.000040	1.000165	1.000374	1.000580	1.000787	1.000993	1.001200	1.001406	1.001611	1.001818	1.002022
278.0	1.000047	1.000172	1.000391	1.000591	1.000799	1.001006	1.001211	1.001416	1.001622	1.001827	1.002032
277.5	1.000057	1.000181	1.000388	1.000598	1.000807	1.001015	1.001222	1.001427	1.001634	1.001839	1.002044
277,0	1.000059	1.000186	1.000395	1.000605	1.000812	1.001022	1.001228	1.001435	1.001642	1.001848	1.002053
276.5	1.000058	1.000183	1.000393	1.000603	1.000810	1.001019	1.001230	1.001436	1.001642	1.001849	1.002055
276.0	1.000052	1.000178	1.000388	1.000598	1.000807	1.001016	1.001224	1.001430	1.001638	1.001846	1.002053
275.5	1.000042	1.000168	1.000378	1.000589	1.000800	1.001007	1.001219	1.001425	1.001637	1.001844	1.002051
275.0	1.000026	1.000152	1.000362	1.000572	1.000783	1.000992	1.001201	1.001416	1.001618	1.001825	1.002031

Table 2 Density of aqueous Et_4NBr as a function of concentration and temperature

Temperature (K)	*m* ($mol{\cdot}kg^{-1}$)										
	0.00200	0.00500	0.01000	0.01500	0.02000	0.02500	0.03000	0.03500	0.04000	0.04500	0.05000
	Density ($g{\cdot}cm^{-3}$)										
279.0	1.000020	1.000139	1.000333	1.000528	1.000725	1.000917	1.001110	1.001306	1.001496	1.001685	1.001880
278.5	1.000035	1.000152	1.000349	1.000540	1.000735	1.000933	1.001123	1.001316	1.001509	1.001697	1.001893
278.0	1.000040	1.000159	1.000353	1.000548	1.000744	1.000936	1.001132	1.001325	1.001517	1.001706	1.001903
277.5	1.000051	1.000168	1.000365	1.000561	1.000758	1.000952	1.001145	1.001340	1.001533	1.001726	1.001918
277.0	1.000056	1.000175	1.000372	1.000568	1.000763	1.000958	1.001154	1.001349	1.001543	1.001733	1.001929
276.5	1.000051	1.000169	1.000367	1.000564	1.000761	1.000958	1.001155	1.001350	1.001545	1.001734	1.001935
276.0	1.000046	1.000165	1.000363	1.000560	1.000757	1.000953	1.001151	1.001347	1.001541	1.001733	1.001931
275.5	1.000036	1.000155	1.000353	1.000551	1,000747	1.000944	1.001143	1.001339	1.001534	1.001725	1.001925
275.0	1.000018	1.000137	1.000335	1.000533	1.000731	1.000930	1.001128	1.001324	1.001522	1.001710	1.001908

Table 3 Density of aqueous Bu_4NBr as a function of concentration and temperature

Temperature (K)	m (mol·kg^{-1})										
	0.00200	0.00500	0.01000	0.01500	0.01999	0.02499	0.03000	0.03500	0.04000	0.04500	0.05000
	Density (g·cm^{-3})										
279.0	0.999999	1.000080	1.000213	1.000345	1.000477	1.000613	1.000745	1.000879	1.001016	1.001149	1.001282
278.5	1.000009	1.000090	1.000225	1.000360	1.000492	1.000626	1.000761	1.000898	1.001033	1.001167	1.001302
278.0	1.000017	1.000100	1.000233	1.000368	1.000502	1.000637	1.000774	1.000908	1.001045	1.001180	1.001316
277.5	1.000027	1.000108	1.000244	1.000379	1.000516	1.000655	1.000790	1.000925	1.001064	1.001197	1.001333
277.0	1.000031	1.000112	1.000249	1.000386	1.000522	1.000659	1.000795	1.000933	1.001071	1.001209	1.001344
276.5	1.000028	1.000111	1.000248	1.000386	1.000522	1.000660	1.000797	1.000934	1.001074	1.001211	1.001348
276.0	1.000024	1.000107	1.000244	1.000381	1.000520	1.000658	1.000796	1.000934	1.001073	1.001209	1.001350
275.5	1.000013	1.000096	1.000235	1.000376	1.000514	1.000654	1.000794	1.000935	1.001073	1.001209	1.001349
275.0	0.999994	1.000077	1.000217	1.000357	1.000495	1.000635	1.000775	1.000917	1.001057	1.001195	1.001336

Table 4 Density of aqueous $(EtOH)_3EtNBr$ as a function of concentration and temperature

Temperature (K)	m (mol·kg^{-1})											
	0.00100	0.00200	0.00350	0.00476	0.00800	0.01000	0.01250	0.01500	0.01700	0.02000	0.02500	0.03000
	Density (g·cm^{-3})											
279.0	1.000031	1.000115	1.000239	1.000346	1.000622	1.000788	1.001003	1.001214	1.001387	1.001635	1.002054	1.002474
278.5	1.000039	1.000124	1.000252	1.000357	1.000631	1.000797	1.001009	1.001219	1.001387	1.001640	1.002054	1.002472
278.0	1.000044	1.000129	1.000259	1.000365	1.000638	1.000808	1.001017	1.001226	1.001394	1.001643	1.002064	1.002479
277.5	1.000057	1.000141	1.000270	1.000377	1.000654	1.000823	1.001033	1.001246	1.001411	1.001666	1.002091	1.002509
277.0	1.000061	1.000147	1.000275	1,000382	1.000658	1.000827	1.001039	1.001250	1.001421	1.001675	1.002098	1.002519
276.5	1.000058	1.000143	1.000271	1.000379	1.000655	1.000825	1.001038	1.001252	1.001418	1.001673	1.002096	1.002519
276.0	1.000053	1.000138	1.000266	1.000375	1.000651	1.000822	1.001035	1.001248	1.001416	1.001671	1.002095	1.002517
275.5	1.000044	1.000129	1.000259	1.000366	1.000645	1.000816	1.001028	1.001240	1.001413	1.001672	1.002097	1.002517
275.0	1.000026	1.000110	1.000238	1.000345	1.000624	1.000793	1.001008	1.001220	1.001390	1.001644	1.002071	1.002491

Table 5 Variation of $\Delta\theta + 1.074m^{3/2}$ (K) with molality, m, for aqueous solutions of Et_4NBr

m/mol·kg^{-1}	$\Delta\theta + 1.074m^{3/2}$ (K)
0.001999	−0.004
0.005000	−0.016
0.01000	−0.071
0.01500	−0.135
0.02000	−0.157
0.02500	−0.236
0.03000	−0.339
0.03500	−0.383
0.04000	−0.472
0.04490	−0.453
0.05000	−0.517

Table 6 Variation of $\Delta\theta + 1.074m^{3/2}$ (K) with molality, m, for aqueous solutions of Me_4NBr

m/mol·kg^{-1}	$\Delta\theta + 1.074m^{3/2}$ (K)
0.002000	−0.054
0.005000	−0.050
0.009999	0.000
0.01500	−0.115
0.02000	−0.184
0.02500	−0.197
0.03000	−0.285
0.03500	−0.418
0.04000	−0.373
0.04500	−0.421
0.05000	−0.467

Several modifications of the original equation have been proposed [12], including a work by Kaulgud and Pokale [13] that uses the equation proposed by Wakabayashi and Takaizumi [14]:

$$\Delta\theta + 1.074m^{3/2} = K_m m. \tag{2}$$

A plot of $\Delta\theta + 1.074m^{3/2}$ versus m should yield a straight line with a slope equal to Despretz's constant K_m. Blanco and Torres [4] found that the values of the constant differ little from those calculated using Eq. 1. Tables 5 to 8 and Figs. 1 to 4 show the variation of $\Delta\theta + 1.074m^{3/2}$ with molality for all of the systems studied, and Table 9 reports the calculated constants. These values obtained are compared with those of Wada and Miura [15] for the three salts that were studied in common. The values are quite similar in all cases. However, the agreement is not complete, probably due to the fact that Wada and Miura used higher concentrations in their work.

To calculate the ionic contributions to the constant, and following earlier workers such as Wakabayashi and Takaizumi [14], we took a value of $K_m = 6.6$ K·mol^{-1} for the Br^- ion from the report of Kaulgud and Pokale [13]. The calculated values are shown in Table 10.

Kaulgud and Pokale [13], following the method proposed by Leyendekkers in a series of papers [16–21], used values of the "real" radii of ions in aqueous solutions at 298.15 K.

Table 7 Variation of $\Delta\theta + 1.074m^{3/2}$ (K) with molality, m, for aqueous solutions of Bu_4NBr

m/mol·kg^{-1}	$\Delta\theta + 1.074m^{3/2}$ (K)
0.002000	−0.002
0.005000	−0.037
0.01000	−0.126
0.01500	−0.247
0.01999	−0.320
0.02499	−0.407
0.03000	−0.508
0.03500	−0.654
0.04000	−0.696
0.04500	−0.720
0.05000	−0.852

Table 8 Variation of $\Delta\theta + 1.074m^{3/2}$ (K) with molality, m, for aqueous solutions of $(EtOH)_3EtNBr$

m/mol·kg^{-1}	$\Delta\theta + 1.074m^{3/2}$ (K)
0.001000	−0.006
0.002000	−0.018
0.003500	−0.052
0.004762	−0.068
0.008000	−0.139
0.009999	−0.185
0.01250	−0.239
0.01500	−0.266
0.01700	−0.308
0.02000	−0.410
0.02500	−0.541
0.03000	−0.558

These radii are larger than the corresponding Pauling's radii by an amount Δ. According to Kaulgud and Pokale [13], the radii are larger that the Pauling ionic radii (r) by an amount Δ that is defined by the positional correlation of the ion and the adjacent water molecules.

Using the measured densities at 277.15 K we calculated the limiting partial molar ionic volumes using Conway's method [22]. A plot of the partial molar volumes at infinite dilution $\overline{V^{\circ}}$ versus molar mass allows the calculation of $\overline{V^{\circ}}$ for the anion. Then, using the additivity principle, $\overline{V^{\circ}}$ is obtained for each cation. From these values it is possible to obtain the effective radii for the cations. Several workers [23–31] have used the semi-empirical equation:

$$V^{\text{o}}_{\text{ion}} = 2.5(r + \Delta)^3 \tag{3}$$

that we also used here to get the values reported in Table 11. In reference [13], a plot of $K_{m(\text{ion})}$ versus $(r + \Delta)$ is presented. It was found that the values for the tetraalkylammonium cations deviate from a linear tendency as shown in Fig. 5. The deviations were attributed partially to the fact that no values for the volumes at 277.15 K were known at the time, even though they expected there to be a small correction. According to our results, when using

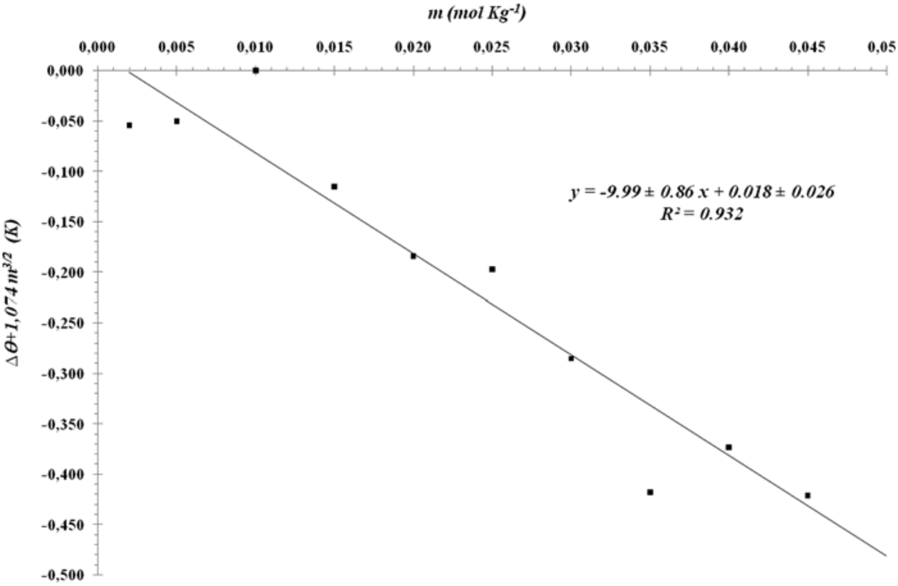

Fig. 1 Plot of $\Delta\theta + 1.074m^{3/2}$ against molality (m/mol·kg^{-1}) for aqueous solutions of Me_4NBr

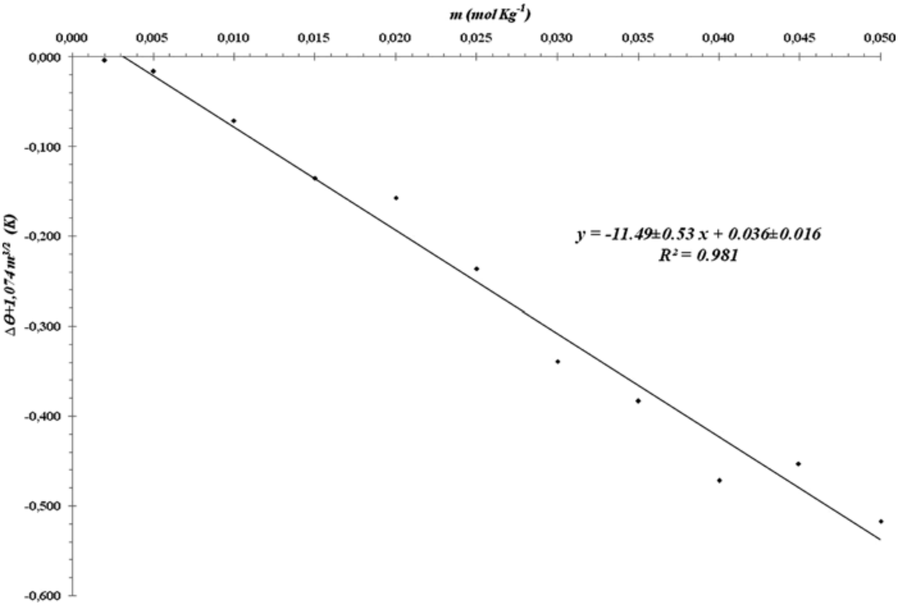

Fig. 2 Plot of $\Delta\theta + 1.074m^{3/2}$ against molality (m/mol·kg^{-1}) for aqueous solutions of Et_4NBr

values of volumes determined at temperatures in the neighborhood of the temperature of maximum density, the tetraalkylammonium cations still deviate from a straight line.

In Fig. 5 the filled triangles represent the experimental results reported in Ref. [13] and the open ones are the results of this work. There is a small difference as had been predicted

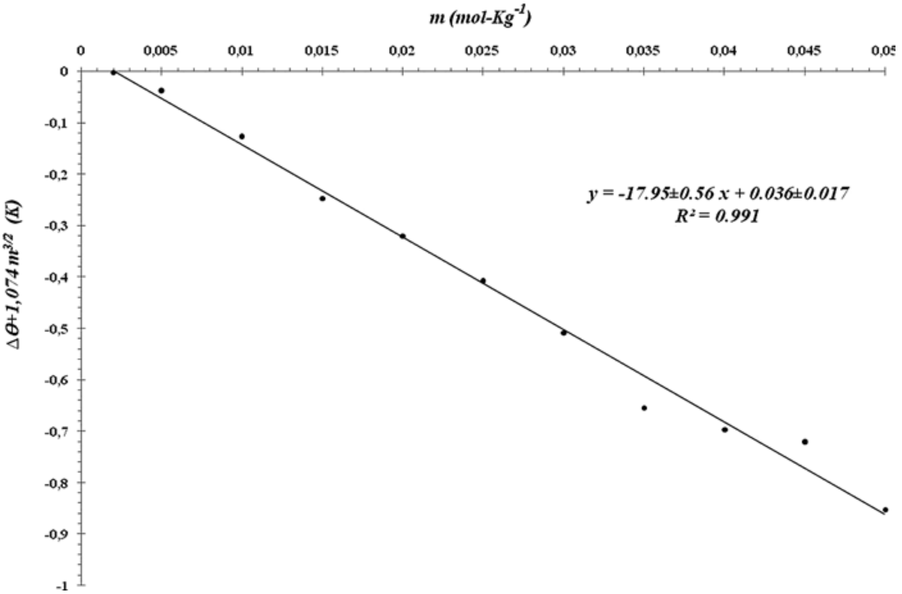

Fig. 3 Plot of $\Delta\theta + 1.074m^{3/2}$ against molality (m/mol·kg^{-1}) for aqueous solutions of Bu_4NBr

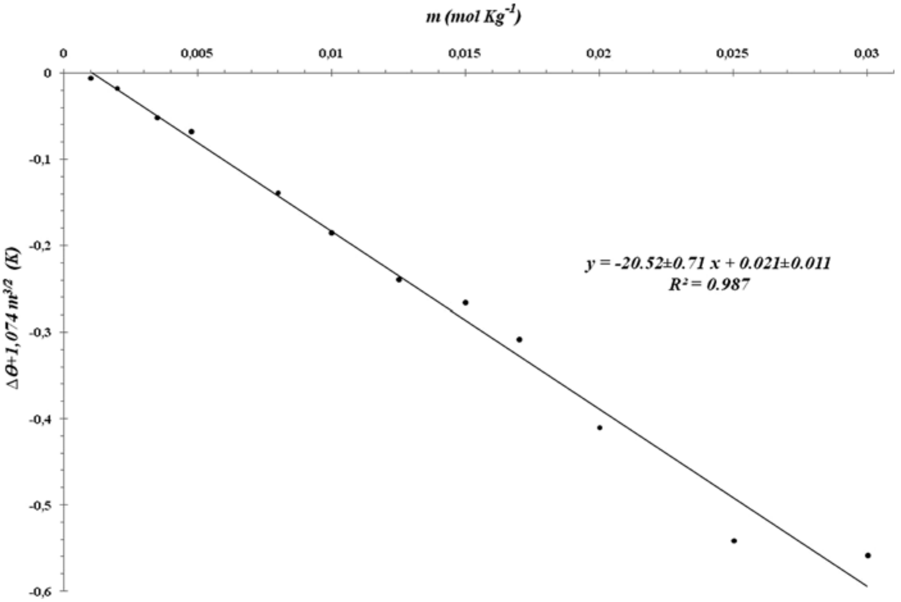

Fig. 4 Plot of $\Delta\theta + 1.074m^{3/2}$ against molality (m/mol·kg^{-1}) for aqueous solutions of $(EtOH)_3EtNBr$

earlier [4, 13]. In Ref. [13], density data at 298.15 K were used because at that time data were not available at lower temperatures. We used our data in the vicinity of 277.15 K and thus, the values of the calculated radii are slightly lower that those reported earlier. As we had pointed out before [4], the simplest prediction of the effect of the tetraalkylammonium

Table 9 Despretz constants (K·mol^{-1}·kg)

	Me_4NBr	Et_4NBr	Bu_4NBr	$(EtOH)_3EtNBr$
K_m[a]	−10.10	−11.47	−17.93	−20.48
K_m[b]	−9.86	−11.23	−17.69	−20.30
K_m[c]	−9.9	−11.0	−15.9	–

[a] Calculated using Eq. 1

[b] Calculated using Eq. 2

[c] From [15]

Table 10 Despretz constants K_m (K·mol^{-1}·kg) for individual ions

Ion	Et_4N^+	Me_4N^+	Bu_4N^+	$(EtOH)_3EtN^+$
K_m	−4.85	−3.48	−11.31	−13.86

Table 11 Effective ionic radii of alkylammonium cations

Ion	$r_{Pauling}$ (nm)	$(r + \Delta)$ (nm)[a]	$(r + \Delta)$ (nm)[b]
Me_4N^+	0.305	0.3194	0.3366
Et_4N^+	0.369	0.3816	0.3956
Bu_4N^+	0.468	0.4722	0.4843

[a] This work

[b] From [13]

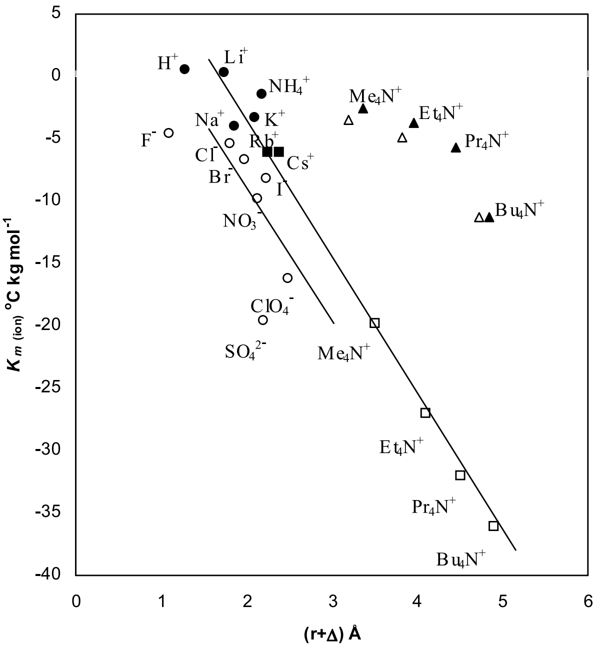

Fig. 5 Variation of the Despretz constant K_m with the effective ionic radii $(r + \Delta)$. Symbols: (●, ■) cations; (○), anions; (□), tetraalkyl ammonium salts calculated according to their size, (▲) Experimental values from Kaulgud and Pokate [13]; (△) this work

cations on the TMD is that they should increase its value, because the cations are supposed to be water structure makers. In fact this does not happen: as shown in this work, among others, and $\Delta\theta$ is negative in all cases. Some authors, for instance Darnell and Greyson [12], propose that at lower temperatures near the TMD the structural effect is the opposite. That is, it changes sign. This is not in agreement with experimental observations [13]. Earlier reports in the literature [4, 13] show that the change in sign does not happen. This work shows clearly that the values of the calculated radii support the conclusion that the tetrabutylammonium cations enhance the water structure at temperatures in the neighborhood of the TMD.

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