

Limiting partial molar volumes and expansions for triethylamine in water and in aqueous tetraethylammonium chloride solutions from 15 to 35 °C

Isabel M. S. Lampreia* and José M. S. T. Neves

Centro de Ciência e Tecnologia de Materiais and ICAT, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Ed. C1, 1700, Lisboa, Portugal

The densities of ternary systems of triethylamine in aqueous tetraethylammonium chloride solutions have been measured, at 5 °C intervals from 15 to 35 °C, with a vibrating tube densimeter. The molalities in tetraethylammonium chloride studied were 0, 0.05, 0.4 and 0.9 mol kg⁻¹. The concentration of triethylamine was varied from 0 to *ca.* 0.35 mol kg⁻¹ in each solvent. Negative excess molar volumes, V_m^E , were obtained for all the systems and their variations with the amine mole fraction were fitted to the Redlich–Kister equation. Limiting partial molar volumes and expansions of triethylamine, $V_{Et_3N}^\infty$ and E_{P, Et_3N}^∞ , were evaluated using the derivatives dV_m^E/dx_{Et_3N} and $dV_{Et_3N}^\infty/dT$, respectively. Values of $V_{Et_3N}^\infty$ increase with temperature for all the solvents. Limiting excess partial molar volumes of triethylamine, $V_{Et_3N}^{E, \infty}$, are considerably negative and decrease with the salt concentration. This means a shift from ideality in the direction of a better packing efficiency of Et₃N in the cage structure of the water and this effect increases as the concentration of the salt is increased. Values of E_{P, Et_3N}^∞ are all positive and increase with the salt concentration. This may signify that the accommodation of Et₃N in the water structure decreases with temperature. Molar expansions were also derived and plotted *vs.* the amine concentration.

Systematic volumetric studies in binary mixtures have been undertaken in order to gain information about intermolecular interactions and changes in packing efficiencies with composition.^{1–6}

Since a significant portion of the measurements have been made in water, a couple of structural interaction models,^{7,8} based on various concepts of the water structure, have been proposed to explain the experimental results. In aqueous solutions of non-electrolytes the concept of hydrophobic interactions^{9,10} has been largely used.

The extension of these studies to ternary solutions is considered very important, since the addition of a third component to a mixed solvent can be used to produce convenient structural modifications in the solvent, with useful industrial applications.^{11,12}

In particular, mixed-solvent electrolytes, have been intensely studied owing to their potential application in industry, namely in the field of extractive distillation,¹³ where the salt acts as a useful mass separating agent. In addition, mixed solvents occur in many biological fluids and are intermediate products in several industrial processes.

The alteration of the phase equilibrium produced in a non-electrolyte mixture due to the presence of salts is known as the salt effect. Salting in and salting out corresponds, respectively, to an increase and a decrease of the volatility of the non-electrolyte due to the presence of the salt.

Volumetric studies and, in particular, determinations of volume derivatives with respect to temperature and pressure, have proved to be very sensitive to the effect of a particular substance on the water structure,^{5,6,14,15} and as a consequence on the packing efficiency.

In the present paper, as a part of our thermodynamic studies on mixed solvents^{16,17} and the salt effect,¹⁸ we report precise density measurements, at 15, 20, 25, 30 and 35 °C, for solutions of Et₃N in water and in aqueous Et₄NCl solutions at three different concentrations, up to *ca.* 0.9 mol kg⁻¹.

Data were reduced to excess molar volumes and partial molar volumes and expansions of Et₃N at infinite dilution were derived, giving useful information concerning the nature of the interactions of Et₃N with water in the presence of an

electrolyte with a hydrophobic moiety similar to that of the amine. The effects of temperature and amine concentration, on the above thermodynamic properties were also explored, to obtain more information concerning changes in the water structure.

Experimental

Materials

Tetraethylammonium chloride (purity > 98 mass%, *ca.* 2% H₂O) was purchased from Fluka and used without further purification. It was dried at 80 °C in a vacuum oven for at least 3 days immediately prior to weighing. Triethylamine was supplied by Merck and submitted to three fractional distillations. Details of the procedure followed have been described previously.¹⁹ Its purity was tested by density measurements ($d = 723.00$ kg m⁻³ at 25 °C). Literature values reported at the same temperature are 723.18 kg m⁻³,²⁰ and 723.01 kg m⁻³.¹⁹

High-purity water was ion exchanged (18 MΩ cm) from a Milli-Q reagent grade system, supplied by Millipore.

Cyclohexane and chlorobenzene were Merck *pro analysi* products (quoted purity > 99%). The former was fractionally distilled under metallic sodium and the latter was used without further purification. Nitrogen gas was supplied by Linde (quoted purity > 99.9993, vol.%).

Measurements

Solution densities were measured with an Anton Paar Model DMA 60/602 vibrating tube densimeter. The instrument was calibrated with nitrogen, water and two organic solvents, cyclohexane and chlorobenzene, the densities of which had been determined picnometrically. A linear relation between the density of the fluid and the square of the vibrating period ($\rho = A + B\tau^2$) was assumed. As continuous small drifts in the periods of the calibrating fluids were observed, the densimeter was calibrated after each set of three sample measurements. The reproducibility of the measurements was found to be 1×10^{-2} kg m⁻³.

Temperature control of the densimeter was achieved using a circulating water bath, regulated to $\pm 0.005^\circ\text{C}$, at each operating temperature, using a proportional temperature controller. The temperature was calibrated to $25.000 \pm 0.005^\circ\text{C}$ with a precision platinum resistance thermometer (SPRT), previously calibrated by the National Physical Laboratory using the international temperature scale ITS-90.

Three aqueous Et_4NCl stock solutions (later used as solvents) were prepared by volume in 2 l volumetric flasks and their exact molalities (0.0572 , 0.4431 and $0.8915 \text{ mol kg}^{-1}$) were determined by density measurements, at 25°C , and by interpolation from a third-degree polynomial calibration curve. The equation of the calibration curve, d vs. $m_{\text{Et}_4\text{NCl}}$, was obtained by rigorously preparing by weight 30 aqueous Et_4NCl solutions with concentrations ranging from 0.009 to 0.9 mol kg^{-1} . The standard deviation of the fit was found to be $3 \times 10^{-5} \text{ mol kg}^{-1}$.

Four series of working solutions were prepared by weight, adding Et_3N to pure water or to the three aqueous tetraethylammonium chloride stock solutions. The working solutions were prepared in 150 ml volumetric flasks which were particularly designed to prevent evaporation.

Corrections for the buoyancy effect have been taken into account in the calculation of the concentration of the solutions.

Results and Discussion

Densities

The experimental density values for the triethylamine solutions in water and in the three different aqueous tetraethylammonium chloride solutions, from 15 to 35°C , have been fitted to an equation of the form

$$d = \sum_{i=0}^2 a_i m^i \quad (1)$$

where a_i are solvent-dependent empirical parameters. These parameters, determined from least-squares analysis of the data, are listed in Table 1, along with the standard deviation of the fits. The experimental densities of the solvents are also listed which can be compared with the a_0 values.

Excess molar volumes, V_m^E , were calculated directly from density values, using eqn. (2)

$$V_m^E = V_m - V_m^{\text{id}} = \left(\sum_{i=1}^2 x_i M_i \right) / \rho - \sum_{i=1}^2 (x_i M_i / \rho_i^*) \quad (2)$$

where V_m and V_m^{id} are the real and ideal molar volumes of the solutions, ρ their density and M_i , x_i and ρ_i^* the molar mass, the molar fraction and density of the two pure components, i.e. Et_3N (component B) and pure water or aqueous Et_4NCl solutions of fixed composition (component A).

Densities used for component A were the experimental values listed in Table 1. For component B the experimental density values 732.16 , 727.70 , 723.00 , 718.67 and 714.41 kg m^{-3} were used for the 15 , 20 , 25 , 30 and 35°C solutions, respectively.

Values of V_m^E were least-squares fitted to Redlich–Kister equations of the form

$$V_m^E = b x_A x_B \quad (3)$$

where b is a constant. Values of b along with their standard deviations and the standard deviation, σ , of the fits are presented in Table 2. As can be seen, the b values are all negative indicating that the shift from ideality is in the direction of a better packing efficiency of Et_3N in the cage structure of the water. As the quadratic term of eqn. (3) is almost negligible in the concentration and temperature ranges studied, (maximum x_B value is 0.0074) the V_m^E dependence on amine concentration is approximately linear apparently indicating that no specific solute–solute interaction is operating over those ranges.

Alternatively, quantitative information about solute–solvent interactions can be obtained from limiting partial molar excess volumes of Et_3N . In order to obtain these values, in all the solvents studied, we have used the well known relationship,²¹

$$V_{\text{Et}_3\text{N}}^E = V_m^E + (1 - x_B)(\partial V_m^E / \partial x_B)_{T,P} \quad (4)$$

where $V_{\text{Et}_3\text{N}}^E$ is the partial molar excess volume of triethylamine. Using eqn. (3) to calculate $(\partial V_m^E / \partial x_B)_{T,P}$ and substituting in eqn. (4) gives eqn. (5)

$$V_{\text{Et}_3\text{N}}^E = b - 2x_B b + b x_B^2 \quad (5)$$

leading to limiting excess partial molar volumes, $V_{\text{Et}_3\text{N}}^{E,\infty} = b$, which are plotted in Fig. 1, as a function of temperature. Lim-

Table 1 Empirical parameters of the equation $d/\text{kg m}^{-3} = \sum_{i=0}^2 a_i m^i$ for Et_3N in pure water and in aqueous Et_4NCl solutions from 15 to 35°C

solvent ^a	$T/^\circ\text{C}$	$a_0/\text{kg m}^{-3}$	$a_1/\text{kg}^2 \text{ m}^{-3} \text{ mol}^{-1}$	$a_2/\text{kg}^3 \text{ m}^{-3} \text{ mol}^{-2}$	$10^2 \sigma^b/\text{kg m}^{-3}$	$d_0(\text{exptl})^c/\text{kg m}^{-3}$
pure water	15	999.152	−15.018	−6.6	3	999.10
	20	998.252	−15.476	−3.8	6	998.20
	25	997.087	−17.207	2.3	5	997.04
	30	995.705	−16.692	−0.4	2	995.64
	35	994.076	−15.507	−5.3	4	994.03
$\text{Et}_4\text{NCl}(0.05)$	15	999.284	−17.312	3.9	1	999.21
	20	998.408	−16.411	—	3	998.38
	25	997.201	−16.728	—	3	997.17
	30	995.840	−17.144	—	3	995.78
	35	994.246	−17.481	—	2	994.20
$\text{Et}_4\text{NCl}(0.44)$	15	999.800	−14.891	—	3	999.73
	20	998.768	−14.373	—	2	998.70
	25	997.401	−14.836	—	2	997.36
	30	995.973	−15.529	—	2	995.86
	35	994.311	−15.902	—	3	994.21
$\text{Et}_4\text{NCl}(0.89)$	15	1001.021	−11.765	—	3	1001.07
	20	999.875	−12.763	—	4	999.86
	25	998.297	−13.296	—	2	998.32
	30	996.671	−14.078	—	3	996.69
	35	994.938	−16.646	—	3	994.87

^a Quantities in parentheses, here and in the other tables, are approximate Et_4NCl concentrations of the solvents in mol kg^{-1} . ^b Standard error of solution density estimation. ^c Experimentally determined density of the solvent.

Table 2 Values of the b parameter of eqn. (3) and limiting partial molar volumes, $V_{\text{Et}_3\text{N}}^\infty$, for Et_3N in pure water and in aqueous Et_4NCl solutions from 15 to 35 °C

solvent	$T/^\circ\text{C}$	$b = V_{\text{Et}_3\text{N}}^{\text{E},\infty}/10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$V_{\text{Et}_3\text{N}}^\infty/10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$\sigma_{\text{fit}}/10^{-6} \text{ m}^3 \text{ mol}^{-1}$
pure water	15	-20.91 ± 0.15	117.28	0.001
	20	-21.29 ± 0.20	117.80	0.002
	25	-21.53 ± 0.10	118.47	0.001
	30	-22.16 ± 0.11	118.81	0.001
	35	-22.78 ± 0.22	119.00	0.002
$\text{Et}_4\text{NCl}(0.05)$	15	-20.63 ± 0.06	117.56	0.001
	20	-21.03 ± 0.07	118.06	0.001
	25	-21.47 ± 0.07	118.53	0.001
	30	-21.80 ± 0.09	119.08	0.001
	35	-22.01 ± 0.08	119.77	0.001
$\text{Et}_4\text{NCl}(0.44)$	15	-23.19 ± 0.12	115.01	0.001
	20	-23.24 ± 0.16	115.85	0.001
	25	-23.51 ± 0.08	116.49	0.002
	30	-23.58 ± 0.16	117.30	0.001
	35	-23.78 ± 0.19	118.00	0.002
$\text{Et}_4\text{NCl}(0.89)$	15	-24.96 ± 0.04	113.23	0.001
	20	-25.00 ± 0.06	114.09	0.001
	25	-24.88 ± 0.03	115.12	0.000
	30	-24.84 ± 0.10	116.04	0.001
	35	-25.09 ± 0.09	116.69	0.001

iting partial molar volumes, $V_{\text{Et}_3\text{N}}^\infty$, obtained by adding the molar volume of pure Et_3N to b , are also listed in Table 2. The method used to obtain $V_{\text{Et}_3\text{N}}^\infty$, based on excess volumes, might be less accurate than an alternative based on apparent molar volumes, V_ϕ . This latter method has already been applied to the system $\text{Et}_3\text{N}-\text{H}_2\text{O}$ ^{2,16} at 25 °C, using a correction for hydrolysis of the amine. The value of $V_{\text{Et}_3\text{N}}^\infty$ obtained in this work, for this same system, at the same temperature, is *ca.* 2% lower than the values obtained in ref. 2 and 16. Such a difference is acceptable since no correction for hydrolysis was applied here, where comparative results, in relation to the different solvents, are of more importance. Moreover a different temperature scale (ITS-90 instead of IPTS-68) was used in the present work.

As can be seen in Table 2, $V_{\text{Et}_3\text{N}}^\infty$ increases, as expected, with temperature in all the solvents studied.

Fig. 1 shows that the $V_{\text{Et}_3\text{N}}^{\text{E},\infty}$ values are all negative and are considerable. A logical explanation based on a hard-sphere approach,^{16,22} is that the large changes in volume, observed when Et_3N is transferred from its pure state to water or aqueous salt solvents, are mainly due to an enhancement of

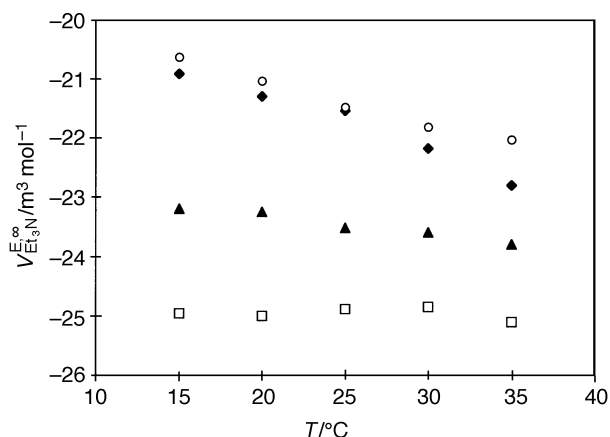
the packing efficiency of this solute in water and in the aqueous salt solvents, in relation to the pure solute. The large difference in the mean size between the solute and the solvent molecules is presumed to be the main reason for this.

Moreover the trends in excess volumes, also shown in Fig. 1, namely the decrease in $V_{\text{Et}_3\text{N}}^{\text{E},\infty}$ with concentration of the salt can be attributed to an increase of the steric fit between Et_3N and the enhanced cage structure of the water, produced by the hydrophobic tetraethylammonium cation. A further point that should be noted, is that the effect of temperature decreases drastically as the salt concentration increases. This feature complies with the increasing tendency towards the stabilisation of the water structure† caused by the hydrophobic moiety of the tetraethylammonium cation. In pure water and in dilute solvents the influence of temperature is in agreement with the expected equilibrium displacement between structured and unstructured water, in the direction of unstructured water, as the temperature increases.

In spite of the fact that a plausible interpretation of $V_{\text{Et}_3\text{N}}^\infty$ and $V_{\text{Et}_3\text{N}}^{\text{E},\infty}$ can be given in terms of packing efficiencies and steric fits due to a cooperative cage effect in aqueous Et_4NCl solvents, these volumetric properties scarcely reveal information about the hydration process, since their values depend on reference values, in this case molar volumes.

The limiting partial molar expansion, $E_{\text{P},\text{Et}_3\text{N}}^\infty = (\partial V_{\text{Et}_3\text{N}}^\infty / \partial T)_P$, reflects directly the hydration process, provided that the intrinsic volume can be taken as temperature independent. Positive values of this quantity indicate a decrease with temperature of the hydration process, giving rise to negative $V_{\text{Et}_3\text{N}}^{\text{E},\infty}$ values, reflecting an increase in regions of low density due to the displacement of the equilibrium between the structured and unstructured water towards structured water (in the case of application of the two-structure model for liquid water⁸).

On the other hand, excess partial molar expansions, at infinite dilution, $E_{\text{P},\text{Et}_3\text{N}}^{\text{E},\infty}$ or an equivalent measure $(\text{d}V_\phi/\text{d}T - \text{d}V_\text{B}/\text{d}T)$, where V_ϕ is the apparent specific volume of the solute in solution and V_B is the specific volume of the pure solute) have been used to study the influence of a number of

**Fig. 1** Excess partial molar volumes of Et_3N , at infinite dilution, in water and in aqueous Et_4NCl solutions, from 15 to 35 °C. ◆, Pure water; ○, 0.05; ▲, 0.44 and □, 0.89 mol kg⁻¹ Et_4NCl .

† Stabilisation of the water structure implies that the number of water molecules involved in regions of low density (clusters, or ice-like structures) increases upon the addition of the solute.

electrolytes on the water structure.^{23,24} It has been accepted that positive values of these quantities indicate structure breaking solutes, whereas negative values indicate structure making solutes.

In spite of the rather limited range of temperature studied in this work, the internal consistency of the data allowed us to obtain fairly reliable values of $E_{P, \text{Et}_3\text{N}}^\infty$ in pure water and in the three aqueous Et_4NCl solvents, by considering a linear dependence of $V_{\text{Et}_3\text{N}}^\infty$ with temperature. Results are presented in Table 3, together with the standard deviation of the least-squares fitting parameters. Kaulgud *et al.*,²³ obtained $E_{P, \text{Et}_3\text{N}}^\infty = -6.8 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ for Me_3N (trimethylamine) in pure water. Our value, for Et_3N in pure water, seems to be consistent with the result for Me_3N since, as the above authors concluded, $E_{P, \text{Et}_3\text{N}}^\infty$ for compounds with the same functional group, should decrease with increasing hydrophobic chain length.

In our case $E_{P, \text{Et}_3\text{N}}^\infty$ is positive in all the solvents studied and increases with the salt concentration. This signifies that, as the temperature is increased, the accommodation of Et_3N in the water structure decreases as expected. The similarity of the $E_{P, \text{Et}_3\text{N}}^\infty$ values between the more concentrated solvents and the pure solute is probably due to the fact that the intermolecular interactions between Et_3N and its neighbouring molecules are of the same type in each case.

We further noted that, whereas in the two more concentrated solvents, $E_{P, \text{Et}_3\text{N}}^\infty$ did not vary with temperature, in pure water and in the more dilute solvent the addition of a quadratic temperature term improved considerably the quality of the $V_{\text{Et}_3\text{N}}^\infty$ vs. T correlation, leading to significant values of $(\partial^2 V_{\text{Et}_3\text{N}}^\infty / \partial T^2)_P$; $(-5.6 \pm 1.8) \times 10^{-9}$ and $(2.6 \pm 0.8) \times 10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-2}$, respectively.

In accordance with the classification of solutes by Hepler,²⁵ based on the following equation,

$$T(\partial^2 V_B^\infty / \partial T^2)_P = -(\partial C_{P, B}^\infty / \partial P)_T \quad (6)$$

where $C_{P, m, B}^\infty$ is the limiting partial molar heat capacity of solute B; negative and positive values of $(\partial^2 V_B^\infty / \partial T^2)_P$ would, respectively, represent structure breaking and making solutes. In our case, and in a somewhat speculative manner, the values referred to above seem to indicate that Et_3N behaves as a structure breaking solute upon infinite dilution in water, and by contrast as a structure making solute in aqueous $0.05 \text{ mol kg}^{-1} \text{ Et}_4\text{NCl}$ under the same conditions. The first part of this tentative conclusion is in accord with an earlier proposal by one of us,¹⁶ that in spite of the large negative value observed for the limiting partial molar excess volume of Et_3N in water, the application of a purely geometric model showed that there was an inefficiency of packing, explained by a possible disruption of the water structure by the amine group, orienting the water molecules in such a way as to decrease the geometrical fit in its vicinity.

Negative values of $E_{P, \text{Et}_3\text{N}}^\infty$, except for the more concentrated solvent, are observed and are listed in Table 3. These values are also consistent with our previous conclusions and the suggestion of Neal and Goring²⁴ and Kaulgud *et al.*,²³ as to the

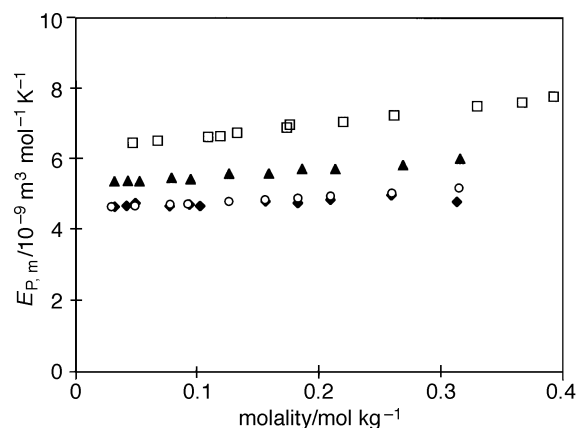


Fig. 2 Molar expansions vs. molality for Et_3N in water and in aqueous Et_4NCl solutions at 25°C . \blacklozenge , Pure water; \circ , 0.05; \blacktriangle , 0.44 and \square , $0.89 \text{ mol kg}^{-1} \text{ Et}_4\text{NCl}$.

structure making ability of Et_3N in water. For the aqueous $0.89 \text{ mol kg}^{-1} \text{ Et}_4\text{NCl}$ solution, the small positive value of $E_{P, \text{Et}_3\text{N}}^\infty$ may signify that the spheres of influence of Et_3N and the tetraethylammonium cation overlap, leading to an equivalent amount of unstructured water with a larger molar expansion.

As is known, transfer functions are also very relevant in the study of structural interactions since they eliminate the need to use reference states. In our case, limiting partial molar expansions of transfer, $\Delta_{tr} E_{P, \text{Et}_3\text{N}}^\infty (\text{H}_2\text{O} \rightarrow \text{Et}_4\text{NCl}_{aq})$, have been calculated and are also listed in Table 3. Increasing positive values of these functions, with increasing salt concentration, also confirms the shift in the equilibrium between open- and close-packed structure of the water towards the open structure.

Considering the influence of amine concentration on the structure of the solutions, estimation of the molar expansions, $E_{P, m} = (\partial V_m / \partial T)_P$ was made, assuming that V_m^E , at a specific composition, can be represented by a quadratic function of the temperature and results for the four solvents, at 25°C , are shown in Fig. 2. This plot shows that the overall effect of adding either Et_4NCl and Et_3N to water is a continuous increase of the molar expansion of the water. For Et_4NCl this behaviour complies with the increasing values of $E_{P, \text{Et}_3\text{N}}^\infty$ as the salt concentration increases. On the other hand the fact that Cl^- is a structure breaking ion²⁶ reinforces the overall effect.

In relation to Et_3N the destructive overlap model⁷ explains the increasing values of the molar expansion upon addition of this solute. The amount of structured water broken down is larger at shorter distances owing to the overlap of the hydration cospheres of Et_3N and Et_4N^+ . As can be seen in Fig. 2 this aspect becomes more important as the salt concentration is increased.

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Table 3 Partial molar and excess partial molar expansions of Et_3N at infinite dilution in pure water and in aqueous Et_4NCl solutions at 25°C and limiting partial molar expansion of transfer from water to the salt solutions

solvent	$b = E_{\text{Et}_3\text{N}}^\infty / 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$	$E_{\text{Et}_3\text{N}}^\infty / 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$	$\Delta_{tr} E_{\text{Et}_3\text{N}}^\infty (\text{H}_2\text{O} \rightarrow \text{Et}_4\text{NCl}) / 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$
pure water	8.9 ± 1.1	-8.3	—
$\text{Et}_4\text{NCl}(0.05)$	11.0 ± 0.5	-6.2	2.1
$\text{Et}_4\text{NCl}(0.44)$	14.9 ± 0.3	-2.3	6.0
$\text{Et}_4\text{NCl}(0.89)$	17.7 ± 0.7	+0.5	8.8
pure Et_3N	17.2 ± 0.1	—	—

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References

- 1 F. J. Millero, *Chem. Rev.*, 1971, **71**, 147.
- 2 S. Cabani, G. Conti and L. Lepori, *J. Phys. Chem.*, 1974, **78**, 1030.
- 3 G. Perron, N. Desrosiers and J. E. Desnoyers, *Can. J. Chem.*, 1976, **54**, 2163.
- 4 G. C. Benson and O. Kiyohara, *J. Solution Chem.*, 1980, **9**, 791.
- 5 M. I. Davis, *Chem. Soc. Rev.*, 1993, **22**, 127.
- 6 G. Douhéret and M. I. Davis, *Chem. Soc. Rev.*, 1993, **22**, 43.
- 7 P. S. Ramanathan, C. V. Krishnan and H. L. Friedman, *J. Solution Chem.*, 1972, **1**, 237.
- 8 A. Ben-Naim, *Water and Aqueous Solutions*, Plenum Press, New York, 1974.
- 9 W. Kauzmann, *Adv. Protein Chem.*, 1959, **14**, 1.
- 10 G. Némethy, *Angew. Chem.*, 1967, **6**, 195.
- 11 W. F. Further, *Thermodynamic Behaviour of Electrolytes in Mixed Solvents*, Advances in Chemistry Series, no. 155, American Chemical Society, Washington, DC, 1976.
- 12 W. F. Further, *Thermodynamic Behaviour of Electrolytes in Mixed Solvents II*, Advances in Chemistry Series, no. 177, American Chemical Society, Washington, DC, 1979.
- 13 Y. Marcus, *Developments in Solvent Extraction*, ed. S. Alegret, Ellis Horwood Series in Analytical Chemistry, West Sussex, 1988.
- 14 Y. Maham, T. T. Teng, L. G. Hepler and A. E. Mather, *J. Solution Chem.*, 1993, **23**, 195.
- 15 J. V. Davis, R. Fooks and Y. Koga, *J. Solution Chem.*, 1993, **23**, 339.
- 16 I. M. S. Lampreia and L. A. V. Ferreira, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3761.
- 17 I. M. S. Lampreia and L. A. V. Ferreira, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 47.
- 18 I. M. S. Lampreia and L. A. V. Ferreira, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1487.
- 19 E. F. G. Barbosa and I. M. S. Lampreia, *Can. J. Chem.*, 1986, **64**, 387.
- 20 T. M. Letcher, *J. Chem. Thermodyn.*, 1972, **4**, 159.
- 21 W. E. Acree Jr., *Thermodynamic Properties of Nonelectrolyte Solutions*, Academic Press, Orlando, FL, 1984.
- 22 B. Lee, *J. Phys. Chem.*, 1983, **87**, 112.
- 23 M. V. Kaulgud, V. S. Bhagde and A. Shrivastava, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 313.
- 24 J. L. Neal and D. A. I. Goring, *J. Phys. Chem.*, 1970, **74**, 658.
- 25 L. G. Hepler, *Can. J. Chem.*, 1969, **47**, 4613.
- 26 F. J. Millero, in *Water and Aqueous solution: Structure Thermodynamics and Transport Processes*, ed. R. A. Horne, Wiley-Interscience, New York, 1972.

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