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Ultrasonic velocities and isentropic compressions of triethylamine in water and in aqueous tetraethylammonium chloride solutions from 15 to 35°C

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Abstract

Ultrasonic velocities in ternary systems of triethylamine in water and in aqueous tetraethylammonium chloride solutions were measured from 15 to 35°C, for molalities in tetraethylammonium chloride from 0 up to 0.9 mol kg^{-1}. The concentration of triethylamine was varied from 0 to ca. 0.35 mol kg^{-1} in pure water and in three concentration-fixed Et_4NCl_{aq} solutions used as solvents.

Isentropic compressibilities, κ_S, were calculated from ultrasonic velocity and density data and fitted to linear functions of molality.

Excess molar isentropic compressions, $K^E_{S,m}$, were estimated and their variations with the amine mole fraction were fitted to the Redlich–Kister equation. Negative values of $K^E_{S,m}$ were obtained for all the systems in the concentration and temperature ranges studied.

Evaluation of triethylamine limiting partial molar isentropic compressions, K^∞_{S,Et_3N}, were thus made for each system, using $dK^E_{S,m}/dx_{Et_3N}$ derivatives.

Negative values of K^∞_{S,Et_3N} were obtained on decreasing the absolute value either with temperature for the same salt concentration or with salt concentration for the same temperature. Apparent molar isentropic compressions of Et_3N, K_{S,ϕ,Et_3N} were also calculated and plotted against amine concentration.

The interpretation of the results based on the changes in packing efficiency and on water structure, complies with and complements the conclusions deduced from limiting partial molar volumes and expansions concerning their variations with temperature and salt concentration. © 1997 Elsevier Science B.V.

Keywords: Ultrasonic velocities; Isentropic compressions; Triethylamine; Chloride

1. Introduction

In our laboratory, we have been studying intermolecular interactions in binary and ternary aqueous and non-aqueous solutions composed by aliphatic amines [1–6]. In a previous work [6], we have reported densities and derived partial molar volumes and expansions of Et_3N at infinite dilution, in water and in Et_4NCl_{aq} solutions. The main goal to be achieved was to detect the changes in packing efficiencies and in the H-bond network of pure water and of water in the mixed solvents composed by water and an

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electrolyte with a hydrophobic moiety similar to the non-electrolyte used as solute.

In this work by combining density data with ultrasonic velocities measured in the same solutions, isentropic compressibilities and derived properties, namely, apparent and limiting partial molar compressions, were determined hopping to complement the previous study. In fact these properties are particularly sensitive to structural interactions [7–9] permitting to add information about the nature of the hydration cosphere of Et_3N infinitely diluted in the above-mentioned solvents.

Consistent information concerning the effect of temperature and salt concentration on structural interactions and in packing efficiency were also obtained.

Our interest in these systems was to study the effect on volumetric properties of structural interactions resulting from the influence of two hydrophobic species, namely, Et_3N and Et_4N^+ with similar tendencies to orient the water molecules.

2. Experimental

2.1. Materials

The origin of and the purification procedure for triethylamine are given elsewhere [1]. Its purity was tested by density measurement. Tetraethylammonium chloride (Purity>98 mass%, ca. 2% H_2O) was purchased from Fluka and used without further purification. It was dried at 80°C in a vacuum stove for at least three days immediately prior to weighing. Water was ion-exchanged (18 MΩ cm) high purity, from Milli-Q reagent grade system, supplied by Millipore.

2.2. Measurements

Ultrasonic velocity measurements were carried out using the sing-around technique. The ultrasonic-pulse repetition rate was measured with a digital Mapco Nusonic sing-around velocimeter (model 6080) supplied with a double transducer system operating at 1.8 MHz. The velocimeter was transformed in order to recover the frequency of the sound wave in order to obtain one more significant digit in the sound velocity. The working method of these velocimeters and the explicit function relating to the repetition rate with the speed of sound were explained in detail by Millero and Kubinsky [10]. The precision and accuracy of the measurements were found to be 0.05 and 0.2 m s^{-1}, respectively.

A tight cell, made of Pyrex glass and specially designed to prevent evaporation, has been used and submerged in a Lauda Compact thermostat KP 20 which was provided with an auxiliary cooling unit model DLK 30. The water bath was controlled within ±0.005°C and measured with a precision platinum resistance thermometer (SPRT), previously calibrated by the National Physical Laboratory in the international temperature scale ITS-90.

The ultrasonic velocimeter was calibrated with degassed pure water from 16 to 30°C by using the data of Del Grosso and Mader [11].

All solutions were prepared by adding weighed quantities of Et_3N to pure water or to three different aqueous tetraethylammonium solutions previously prepared as described in detail in a previous paper [6]. The molalities of the stock solutions, considered as solvents, were determined by density measurements yielding 0.0572; 0.4431 and 0.8915 mol kg^{-1}.

3. Results and discussion

3.1. Ultrasonic velocities and isentropic compressibilities

Table 1 reports our experimental values of ultrasonic velocities, u, for the solutions of triethylamine in water chloride and in three different aqueous tetraethylammonium solutions, from 15 to 35°C at five degree intervals. The results were fitted to equations of the type

$$u = u_0 + Am \tag{1}$$

where u_0 and A are solvent-dependent empirical parameters and m the Et_3N molality.

Isentropic compressibilities at fixed composition, defined by $\kappa_S = (-1/V_m)(\partial V_m/\partial P)_S$ were obtained from ultrasonic velocity and density data [6] using the Newton–Laplace equation

$$\kappa_S = 1/(u^2 d) \tag{2}$$

where d is the density of the solution.

Isentropic compressibilities as function of Et_3N molality in all the solvents at the five temperatures studied are shown in Figs. 1–4. Fig. 5 represents the

Table 1
Ultrasonic velocities of binary and pseudo-binary solutions of Et_3N in pure water and in Et_4NCl_{aq} solutions

Et_3N/H_2O		$Et_3N/Et_4NCl_{aq}(0.05)$		$Et_3N/Et_4NCl_{aq}(0.44)$		$Et_3N/Et_4NCl_{aq}(0.89)$	
(m/mol kg^{-1})	(u/ms^{-1})	(m/mol kg^{-1})	(u/ms^{-1})	(m/mol kg^{-1})	(u/ms^{-1})	(m/mol kg^{-1})	(u/ms^{-1})
15°C							
0.03162	1469.88	0.02869	1478.37	0.03140	1534.46	0.06694	1613.70
0.04149	1471.60	0.04814	1480.88	0.04241	1535.77	0.10822	1619.47
0.04874	1472.26	0.07703	1484.11	0.05212	1537.17	0.11827	1619.03
0.07692	1476.02	0.09154	1486.36	0.07838	1540.81	0.13209	1622.44
0.09312	1478.11	0.12513	1489.93	0.09401	1542.66	0.17278	1624.94
0.10179	1479.55	0.15485	1494.78	0.12552	1546.47	0.21916	1629.32
0.15545	1486.27	0.18182	1497.44	0.15817	1550.68	0.26079	1637.28
0.18187	1489.97	0.20868	1501.11	0.18529	1554.21	0.32905	1639.85
0.20882	1493.35	0.25894	1507.30	0.21270	1558.33	0.36593	1648.31
0.25882	1499.65	0.31400	1514.41	0.26826	1564.37		
0.31255	1506.31			0.31498	1569.87		
20°C							
0.03162	1485.72	0.02869	1493.59	0.03140	1546.90	0.06694	1621.79
0.04149	1487.04	0.04814	1494.59	0.04241	1548.20	0.10822	1626.51
0.04874	1487.83	0.07703	1498.85	0.05212	1549.49	0.11827	1626.10
0.07692	1491.25	0.09154	1500.65	0.07838	1552.55	0.13209	1629.07
0.09312	1493.20	0.12513	1504.63	0.09401	1554.38	0.17278	1631.89
0.10179	1494.33	0.15485	1508.49	0.12552	1557.82	0.21916	1634.27
0.15545	1500.71	0.18182	1511.31	0.15817	1561.62	0.26079	1642.52
0.18187	1504.03	0.20868	1514.51	0.18529	1564.83	0.32905	1644.91
0.20882	1507.18	0.25894	1519.93	0.21270	1567.98	0.36593	1652.27
0.25882	1512.66	0.31400	1526.35	0.26826	1573.48		
0.31255	1518.98			0.31498	1578.95		
25°C							
0.03162	1499.67	0.02869	1507.06	0.03140	1557.78	0.06694	1628.06
0.04149	1500.80	0.04814	1508.68	0.04241	1558.98	0.10822	1632.66
0.04874	1501.60	0.07703	1511.77	0.05212	1559.94	0.11827	1632.34
0.07692	1504.70	0.09154	1513.46	0.07838	1562.68	0.13209	1634.92
0.09312	1506.68	0.12513	1516.79	0.09401	1564.12	0.17278	1637.89
0.10179	1507.52	0.15485	1520.45	0.12552	1567.16	0.21916	1640.27
0.15545	1513.38	0.18182	1523.04	0.15817	1570.65	0.26079	1646.67
0.18187	1516.10	0.20868	1525.99	0.18529	1574.08	0.32905	1648.55
0.20882	1519.00	0.25894	1530.91	0.21270	1576.73	0.36593	1655.58
0.25882	1524.31	0.31400	1536.80	0.26826	1581.54		
0.31255	1529.66			0.31498	1586.04		
30°C							
0.03162	1512.24	0.02869	1518.62	0.03140	1566.51	0.06694	1633.64
0.04149	1512.68	0.04814	1520.47	0.04241	1567.61	0.10822	1637.67
0.04874	1513.38	0.07703	1522.75	0.05212	1568.55	0.11827	1637.15
0.07692	1516.63	0.09154	1524.20	0.07838	1571.16	0.13209	1639.34
0.09312	1517.98	0.12513	1527.41	0.09401	1572.78	0.17278	1641.05
0.10179	1518.87	0.15485	1530.79	0.12552	1575.88	0.21916	1644.43
0.15545	1524.09	0.18182	1532.98	0.15817	1578.61	0.26079	1650.04
0.18187	1526.49	0.20868	1536.03	0.18529	1580.88	0.32905	1651.66
0.20882	1529.05	0.25894	1540.31	0.21270	1583.49	0.36593	1657.32
0.25882	1533.97	0.31400	1545.09	0.26826	1588.23		
0.31255	1539.09			0.31498	1592.15		

Table 1
(Continued)

Et_3N/H_2O		$Et_3N/Et_4NCl_{aq}(0.05)$		$Et_3N/Et_4NCl_{aq}(0.44)$		$Et_3N/Et_4NCl_{aq}(0.89)$	
$(m/\mathrm{mol\,kg^{-1}})$	$(u/\mathrm{ms^{-1}})$	$(m/\mathrm{mol\,kg^{-1}})$	$(u/\mathrm{ms^{-1}})$	$(m/\mathrm{mol\,kg^{-1}})$	$(u/\mathrm{ms^{-1}})$	$(m/\mathrm{mol\,kg^{-1}})$	$(u/\mathrm{ms^{-1}})$
35°C							
0.03162	1522.80	0.02869	1528.19	0.03140	1574.36	0.06694	1637.32
0.04149	1522.84	0.04814	1530.10	0.04241	1575.29	0.10822	1641.04
0.04874	1523.75	0.07703	1532.65	0.05212	1575.98	0.11827	1640.54
0.07692	1526.23	0.09154	1533.62	0.07838	1578.07	0.13209	1642.48
0.09312	1527.77	0.12513	1536.72	0.09401	1579.43	0.17278	1643.85
0.10179	1528.57	0.15485	1539.13	0.12552	1581.98	0.21916	1646.94
0.15545	1533.37	0.18182	1541.15	0.15817	1584.70	0.26079	1651.86
0.18187	1535.29	0.20868	1543.72	0.18529	1586.85	0.32905	1653.25
0.20882	1537.90	0.25894	1548.02	0.21270	1589.75	0.36593	1657.85
0.25882	1541.19	0.31400	1552.46	0.26826	1593.37		
0.31255	1546.32			0.31498	1596.40		

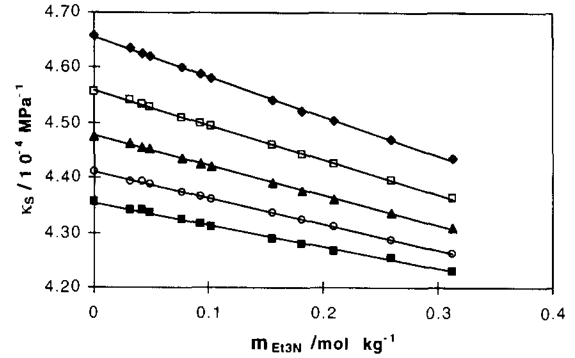

Fig. 1. Isentropic compressibilities vs. molality for Et_3N in pure water from 15 to 35°C: ◆ - 15°C; □ - 20°C; ▲ - 25°C; ○ - 30°C and ■ - 35°C.

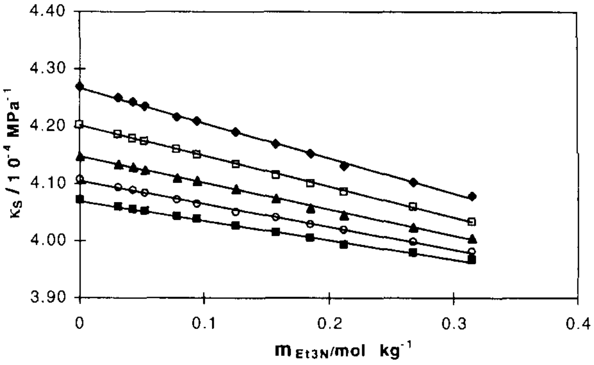

Fig. 3. Isentropic compressibilities vs. molality for Et_3N in Et_4NCl_{aq} (0.44 mol kg^{-1}) from 15 to 35°C: ◆ - 15°C; □ - 20°C; ▲ - 25°C; ○ - 30°C and ■ - 35°C.

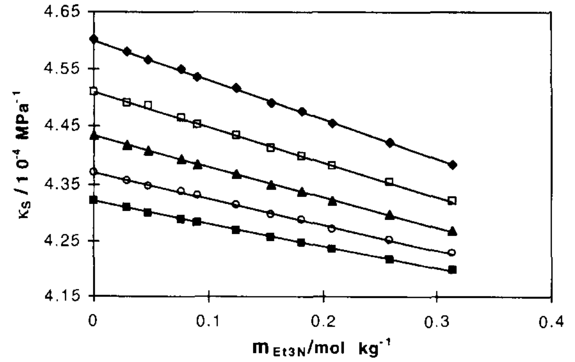

Fig. 2. Isentropic compressibilities vs. molality for Et_3N in Et_4NCl_{aq} (0.05 mol kg^{-1}) from 15 to 35°C: ◆ - 15°C; □ - 20°C; ▲ - 25°C; ○ - 30°C and ■ - 35°C.

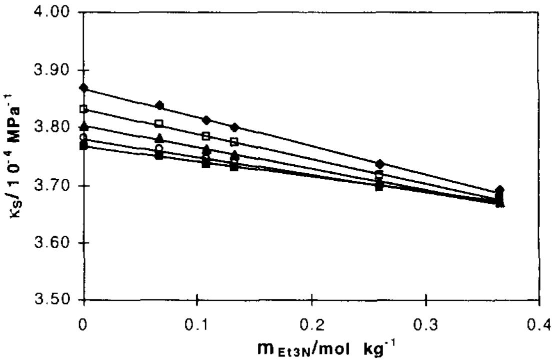

Fig. 4. Isentropic compressibilities vs. molality for Et_3N in Et_4NCl_{aq} (0.89 mol kg^{-1}) from 15 to 35°C: ◆ - 15°C; □ - 20°C; ▲ - 25°C; ○ - 30°C and ■ - 35°C.

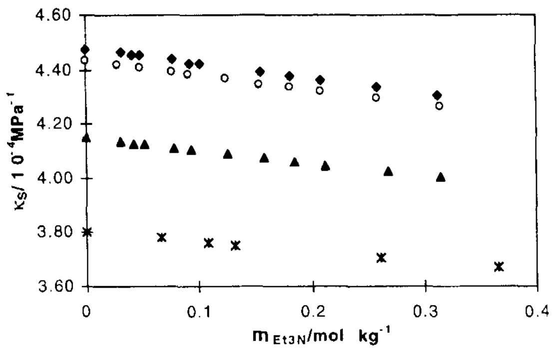

Fig. 5. Isentropic compressibilities vs. molality for Et_3N in pure water and in the three concentration-fixed Et_4NCl_{aq} solution at 25°C: ◆ – pure water; ○ – Et_4NCl_{aq} (0.05 mol kg^{-1}); ▲ – Et_4NCl_{aq} (0.44 mol kg^{-1}) from 15 to 35°C: ◆ -15°C; □ - 20°C; ▲ -25°C; ○ - 30°C and ■ - 35°C.

variation of κ_S with Et_3N molality at 25°C in pure water and in three concentration-fixed Et_4NCl_{aq} solvents.

κ_S values were fitted to linear equations of the form

$$\kappa_S = \kappa_{S,0} + A'm \tag{3}$$

where $\kappa_{S,0}$ and A' are solvent dependent empirical parameters. u_0, A, $\kappa_{S,0}$ and A' parameters were determined by least squares fits of the data and are represented in Table 2 jointly with their standard deviations and the standard deviations of the fits. In the same table we also report the experimental sound velocity in the solvents studied.

As we can see in Table 2, the slopes A' are negative, decreasing in absolute value with temperature. This indicates that as long as we add Et_3N to the water or to the Et_4NCl_{aq} solutions there is an increase of rigidity corresponding to a better packing efficiency.

The linearity of the curves κ_S vs. m_{Et_3N} also seems to indicate that no specific intermolecular interaction exists between triethylamine and any other component of these solutions and that the effect of increasing temperature and salt concentration would be opposite to that of adding the amine to the water.

In Figs. 1–4, we observe that the effect of temperature clearly decreases with both the amine or salt concentration, probably due to the common ability of these two components of the solution to stabilise the structure of the water. In the more concentrated solvent we can also observe that the effect of temperature almost disappears for the bigger amine concentration.

Fig. 5 shows that for the same temperature the compressibility of the solutions decrease in a fairly constant manner with the amine concentration in all the solvents. This fact makes us to suspect that in the ternary solutions the prevailing interactions of Et_3N are with the water.

3.2. *Excess, partial and apparent molar isentropic compressions*

In order to further understand the changes in the water structure produced by the mixture procedure, molar and excess molar isentropic compressions, at fixed composition, defined by, $K_{S,m} = -(\partial V_m/\partial P)_S$, and $K^E_{S,m} = K_{S,m} - K^{id}_{S,m}$, respectively, have been calculated for all the solvents from 15 to 35°C. $K^{id}_{S,m}$ is the ideal molar isentropic compression at the same temperature, pressure and composition of the real mixture.

After Benson and Kiyohara [12], the ideal molar isentropic compression has been calculated using the thermodynamic relation

$$K^{id}_{S,m} = K^{id}_{T,m} - T(E^{id}_{P,m})^2/C^{id}_{P,m} \tag{4}$$

where $K^{id}_{T,m}$ is the ideal molar isothermal compression, $E^{id}_{P,m}$ the ideal molar isobaric expansion and $C^{id}_{P,m}$ the ideal molar isobaric heat capacity. These quantities were obtained using the mixing rule, expressed by Eq. (5).

$$Q^{id}_m = x_A Q^*_{m,A} + x_B Q^*_{m,B} \tag{5}$$

where Q^{id}_m represents $K^{id}_{T,m}$, $E^{id}_{P,m}$ or $C^{id}_{P,m}$, and $Q^*_{m,A}$ and $Q^*_{m,B}$ are the corresponding molar properties of the A and B components, considered as pure water or aqueous Et_4NCl_{aq} solutions of fixed composition, and Et_3N respectively. Values of the molar properties of the A and B components used to derive the ideal molar properties of the solutions are presented in Table 3.

The mixing rule defined in Eq. (5) corresponds to the definition of ideal state in which every component obey the Raoult's law [8].

Excess molar isentropic compressions, thus represent the deviation of the molar isentropic compressions of real binary and pseudo binary mixtures, from the same thermodynamic quantities calculated for the ideal solution just defined.

Table 2
Parameters of the Eqs. (1) and (3) for Et_3N in pure water an in Et_4NCl_{aq} solutions from 15 to 35°C

Solvent	t (°C)	u_0 ($m\ s^{-1}$)	A ($m\ s^{-1}\ mol^{-1}\ kg$)	σ_{fit} [a] ($m\ s^{-1}$)	$\kappa_{S,0}$ ($10^{-4}\ MPa^{-1}$)	A' ($10^{-5}\ MPa^{-1}\ mol^{-1}\ kg$)	σ_{fit} [a] ($10^{-4}\ MPa^{-1}$)	u_0(exp) ($m\ s^{-1}$)
Pure water								
	15	1465.98 ± 0.1	130.0±0.6	0.2	4.6555 ± 0.0010	−7.19 ± 0.06	0.002	1465.95
	20	1482.20 ± 0.1	118.2±0.7	0.2	4.5587 ± 0.0008	−6.30 ± 0.05	0.002	1482.59
	25	1496.56 ± 0.1	106.8±0.7	0.2	4.4774 ± 0.0007	−5.48 ± 0.05	0.001	1496.97
	30	1508.92 ± 0.1	96.8±0.5	0.2	4.4097 ± 0.0010	−4.83 ± 0.06	0.002	1508.90
	35	1519.81 ± 0.2	84.9±1.0	0.3	4.3544 ± 0.0010	−4.02 ± 0.06	0.002	1519.83
Et_4NCl_{aq}(0.05)								
	15	1474.67 ± 0.2	126.3±0.9	0.3	4.6009 ± 0.0010	−6.88 ± 0.06	0.002	1474.73
	20	1489.97 ± 0.2	116.5±1.0	0.4	4.5107 ± 0.0014	−6.10 ± 0.08	0.003	1490.22
	25	1503.86 ± 0.1	105.1±0.6	0.2	4.4334 ± 0.0006	−5.29 ± 0.04	0.001	1503.94
	30	1515.82 ± 0.2	94.4±0.9	0.3	4.3694 ± 0.0008	−4.67 ± 0.05	0.002	1515.84
	35	1525.88 ± 0.2	85.2±0.5	0.2	4.3194 ± 0.0005	−3.97 ± 0.04	0.001	1525.66
Et_4NCl_{aq}(0.44)								
	15	1530.72 ± 0.2	125.9±1.0	0.3	4.2676 ± 0.0011	−6.16 ± 0.07	0.002	1530.75
	20	1543.67 ± 0.1	112.5±0.8	0.2	4.2012 ± 0.0008	−5.36 ± 0.05	0.001	1543.79
	25	1554.74 ± 0.2	100.7±1.0	0.3	4.1472 ± 0.0009	−4.63 ± 0.05	0.002	1554.69
	30	1563.95 ± 0.1	90.9±0.9	0.3	4.1043 ± 0.0010	−4.12 ± 0.06	0.002	1563.73
	35	1571.97 ± 0.2	79.6±1.0	0.3	4.0696 ± 0.0001	−3.39 ± 0.06	0.002	1571.95
Et_4NCl_{aq}(0.89)								
	15	1606.99 ± 0.4	114.9±2.0	0.6	3.8674 ± 0.0021	−4.89 ± 0.11	0.003	1607.03
	20	1615.57 ± 0.3	102.2±1.4	0.4	3.8311 ± 0.0016	−4.22 ± 0.08	0.002	1615.56
	25	1622.96 ± 0.3	90.5±1.6	0.5	3.8024 ± 0.0015	−3.62 ± 0.08	0.002	1623.23
	30	1629.03 ± 0.3	79.3±1.6	0.5	3.7803 ± 0.0015	−3.07 ± 0.08	0.002	1629.01
	35	1633.52 ± 0.5	68.7±1.8	0.5	3.7664 ± 0.0017	−2.56 ± 0.09	0.003	1633.49

[a] Standard deviation of the fit.

Table 3
Characteristic parameters for pure water, Et_4NCl_{aq} solutions and Et_3N from 15 to 35°C [a]

Solvent	t (°C)	$K_{S,m}$ [b] (mm^3 MPa^{-1} mol^{-1})	$E_{P,m}$ [c] (mm^3 K^{-1} mol^{-1})	$C_{P,m}$ [d] (JK^{-1} mol^{-1})	$K_{T,m}$ (mm^3 MPa^{-1} mol^{-1})
Pure water					
	15	8.3982	2.7215	75.403	8.4267
	20	8.2256	3.7341	75.332	8.2824
	25	8.0870	4.6488	75.291	8.1756
	30	7.9820	5.4878	75.271	8.1008
	35	7.8933	6.2683	75.267	8.0541
Et_4NCl_{aq}(0.05)					
	15	8.3671	2.7855	75.71	8.3966
	20	8.2073	3.6908	75.65	8.2601
	25	8.0779	4.5962	75.62	8.1611
	30	7.9736	5.5016	75.60	8.0950
	35	7.8963	6.4069	75.60	8.0637
Et_4NCl_{aq}(0.44)					
	15	8.1919	3.7929	77.74	8.2452
	20	8.0707	4.5742	77.89	8.1495
	25	7.9794	5.3556	77.83	8.0893
	30	7.9111	6.1370	77.85	8.0578
	35	7.8546	6.9183	77.88	8.0440
Et_4NCl_{aq}(0.89)					
	15	7.8630	4.8023	80.03	7.9460
	20	7.7990	5.5810	80.24	7.9128
	25	7.7493	6.3598	80.30	7.8995
	30	7.7196	7.1385	80.39	7.9118
	35	7.7054	7.9173	80.46	7.9455
Solute Et_3N					
	15	132.5	176.59	212.8	174.7
	20	143.6	174.47	215.4	185.0
	25	153.3	170.23	218.1	193.9
	30	166.2	172.35	220.8	206.0
	35	177.7	168.11	223.4	216.6

[a] Values for water were calculated from κ_T and d data taken from [15]. Values for other solvents were calculated from $K_{S,m}$. For Et_3N, the 25°C value was calculated from experimental $K_{S,m}$ of [13]. For other temperatures $K_{T,m}$ was calculated from κ_T at 25°C and temperature coefficient calculated from data of [17].

[b] Derived from experimental κ_S values, determined in this work, except for Et_3N. For Et_3N the 25°C value was calculated from experimental κ_S and d values taken from [13]. For the other temperatures $K_{T,m}$ values were used to derive $K_{S,m}$ using the equation $K_{S,m} = K_{T,m} - T(E_{P,m})^2/C^{id}_{P,m}$

[c] Calculated from data taken from [14] for water and from [6] for the other solvents and Et_3N.

[d] Data for water are from [15]. For the other solvents the 25°C values were calculated using apparent molar heat capacity values taken from [16]. For other temperatures, data from the same Ref. were used but referred to Et_4NClBr. We noticed that the differences between $C_{P,m}$ values related to the two halides at 25°C were 0.01% for the 0.05 and 0.44 mol kg^{-1} solvents and 0.1% for the 0.89 mol kg^{-1} solvent. These differences are not significant for the calculation of the excess compressions.

Excess molar isentropic compressions were then calculated and least squares fitted to Redlich–Kister equations of the form

$$K^{E}_{S,m} = cx_Ax_B \qquad (6)$$

where c is a constant and x_A and x_B are the mole fractions of the solvents and triethylamine, respectively. Parameters associated jointly with the standard deviations as well as the standard deviations of the fits are presented in Table 4.

Table 4
c parameters of Eq. (6) and limiting partial molar compressions, $K^{\infty}_{\mathrm{S,Et_3N}}$, for $\mathrm{Et_3N}$ in water and in $\mathrm{Et_4NCl_{aq}}$ solutions from 15 to 35°C

Solvent	t (°C)	$c = K^{\mathrm{E},\infty}_{\mathrm{S,Et_3N}}$ ($\mathrm{mm^3\,MPa^{-1}\,mol^{-1}}$)	$K^{\infty}_{\mathrm{S,Et_3N}}$ ($\mathrm{mm^3\,MPa^{-1}\,mol^{-1}}$)	σ_{fit} ($\mathrm{mm^3\,MPa^{-1}\,mol^{-1}}$)
Pure water				
	15	−192.3 ± 0.2	−59.8	0.002
	20	−191.8 ± 0.3	−48.2	0.003
	25	−187.7 ± 0.6	−36.4	0.002
	30	−197.0 ± 0.3	−30.7	0.003
	35	−199.1 ± 0.4	−21.5	0.004
$\mathrm{Et_4NCl_{aq}}$(0.05)				
	15	−188.3 ± 0.4	−55.7	0.004
	20	−190.0 ± 0.6	−46.4	0.005
	25	−190.6 ± 0.2	−37.3	0.002
	30	−196.3 ± 0.2	−30.1	0.002
	35	−199.1 ± 0.4	−21.6	0.002
$\mathrm{Et_4NCl_{aq}}$(0.44)				
	15	−188.3 ± 0.4	−51.8	0.003
	20	−185.4 ± 0.3	−41.7	0.003
	25	−187.1 ± 0.3	−33.4	0.003
	30	−193.9 ± 0.4	−27.1	0.004
	35	−195.8 ± 0.3	−18.2	0.002
$\mathrm{Et_4NCl_{aq}}$(0.89)				
	15	−170.5 ± 1.1	−38.0	0.01
	20	−174.2 ± 1.1	−30.6	0.01
	25	−175.9 ± 0.9	−22.6	0.01
	30	−182.8 ± 0.8	−16.6	0.01
	35	−186.9 ± 0.7	−9.2	0.01

Limiting excess partial molar compressions of $\mathrm{Et_3N}$, $K^{\mathrm{E},\infty}_{\mathrm{S,Et_3N}}$, in all the solvents and temperatures studied were derived using the well-known thermodynamic relation [18] expressed by Eq. (7)

$$K^{\mathrm{E}}_{\mathrm{S,Et_3N}} = K^{\mathrm{E}}_{\mathrm{S,m}} + (1 - x_i)(\mathrm{d}K^{\mathrm{E}}_{\mathrm{S,m}}/\mathrm{d}x_i) \qquad (7)$$

Substituting $K^{\mathrm{E}}_{\mathrm{S,m}}$ by the expression of Eq. (6) and using it to calculate $\mathrm{d}K^{\mathrm{E}}_{\mathrm{S,m}}/\mathrm{d}x_{\mathrm{Et_3N}}$, we obtain

$$K^{\mathrm{E}}_{\mathrm{S,Et_3N}} = c_1 - 2x_{\mathrm{Et_3N}}c_1 + c_1x^2_{\mathrm{Et_3N}} \qquad (8)$$

leading to limiting excess partial molar isentropic compressions $K^{\mathrm{E},\infty}_{\mathrm{S,Et_3N}} = c$. Limiting partial molar isentropic compressions, $K^{\infty}_{\mathrm{S,Et_3N}}$, obtained by adding to the c values the molar compression of pure $\mathrm{Et_3N}$, are also presented in Table 4.

As we can see in this table, all values of $K^{\infty}_{\mathrm{S,Et_3N}}$ are negative, indicating that the solvent near $\mathrm{Et_3N}$ molecules, infinitely diluted in it, is more incompressible than in the bulk. This is in the hypotheses of $\mathrm{Et_3N}$ itself being incompressible. It can also be seen in that table that values of $K^{E,\infty}_{S,Et_3N}$ increase as the salt concentration and temperature increase, leading to $K^{\infty}_{\mathrm{S,Et_3N}}$ values which also increase with the above referred factors. This signify that the cause giving rise to the increasing of rigidity of the solvent close to the solute in relation to the solvent in the bulk decreases with temperature and salt concentration.

In a previous work [6], we found that the limiting partial molar volumes, $V^{\infty}_{\mathrm{Et_3N}}$, increased with temperature for each fixed salt concentration and decreased with the salt concentration for fixed temperature. The increase of $V^{\infty}_{\mathrm{Et_3N}}$ with temperature represented by positive limiting partial molar expansion, has been explained by the decrease with temperature of the geometric fitness of $\mathrm{Et_3N}$ infinitely diluted in all the solvents. The reason for this behaviour has been considered to be the decrease of the number of bounded low density water molecules surrounding the solute due to its hydrophobicity with temperature [19]. This reason agrees with the present results which indicate an increase with temperature of the compressibility of the solvent around the solute molecule in relation to the solvent in the bulk. In fact it has been considered that the unbounded water is more compressible than the ice-like bounded one [20].

On the other hand, the increase and decrease of K^{∞}_{S,Et_3N} and $V^{\infty}_{Et_3N}$, respectively, with the concentration of the salt could, at the first sight, be thought to be contradictory. A plausible explanation for this fact is the increasing tendency for cosphere overlapping [21] of the hydration shells of Et_3N and Et_4N^+ as long as the concentration of the salt increases. In this case, the number of bounded water molecules in the neighbourhood of the solute would be less dependent on the magnitude of the overlapping region [22], leading to higher K^{∞}_{S,Et_3N} values.

Since the composition dependence of partial or apparent molar properties has been used to detect the changes in molecular patterns [8,9], we have also calculated the apparent molar compressions and plotted against Et_3N composition.

Excess partial molar isentropic compressions of Et_3N could be obtained, from Eq. (7) by the evaluation of $dK^E_{S,m}/dx_{Et_3N}$ derivatives based on the curve fitting represented by Eq. (6). Calculation of these properties by the procedure just mentioned is not recommended because the smoothing of the $K^E_{S,m}$ data can mask any feature of the composition dependence of that property. Alternatively, point to point calculation of apparent molar compressions, K_{ϕ,S,Et_3N}, based on Eq. (9), has been preferred [8].

$$K_{\phi,S,Et_3N} = (K^E_{S,m}/x_{Et_3N}) + K^*_{Et_3N} \qquad (9)$$

In this equation, K^*_{S,Et_3N} is the molar compression of pure Et_3N.

In Fig. 6, values of K_{ϕ,S,Et_3N} are plotted against Et_3N molar fraction for the five temperatures studied for the Et_4NCl_{aq} solvent at 0.44 mol kg^{-1}, as an example. In Fig. 7, K_{ϕ,S,Et_3N} values for all the solvents are also shown for one of the temperatures studied (20°C as an example). Figs. 6 and 7, show that K_{ϕ,S,Et_3N} is more or less constant for each temperature at fixed salt composition or for each salt composition at fixed temperature, throughout all the concentration range of the amine. While temperature and salt concentration increase, K_{ϕ,S,Et_3N} also increases as expected. The constancy of those values over the amine concentration for all the solvents and temperatures studied points out to a stabilisation of the water structure produced either by the Et_3N molecule in pure water or also by the tetraalkylammonium cation in other solvents.

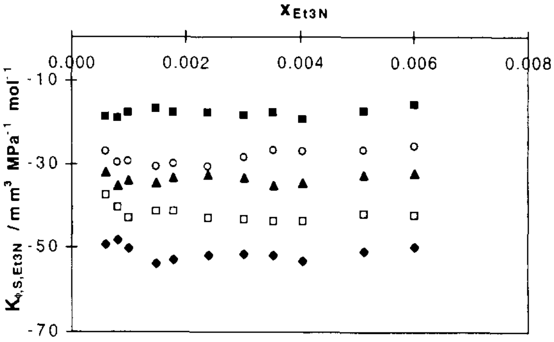

Fig. 6. Apparent molar isentropic compressions vs. mole fraction for Et_3N in Et_4NCl_{aq} (0.44 mol kg^{-1}) from 15 to 35°C: ◆ – 15°C; □ – 20°C; ▲ – 25°C; ○ – 30°C and ■ – 35°C.

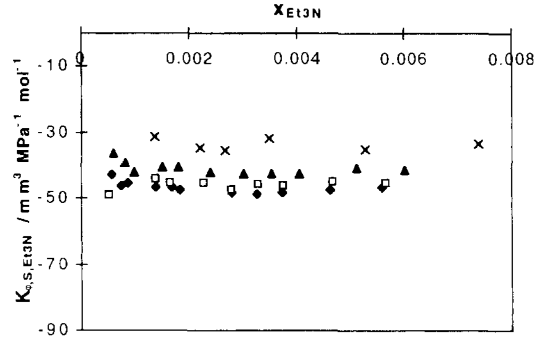

Fig. 7. Apparent molar isentropic compressions vs. mole fraction for Et_3N in pure water and in the three concentration-fixed Et_4NCl_{aq} solutions at 20°C: ◆ – pure water; □ – Et_4NCl_{aq} (0.05 mol kg^{-1}); ▲ – Et_4NCl_{aq} (0.44 mol kg^{-1}) and X Et_4NCl_{aq} (0.89 mol kg^{-1}).

4. Conclusions

Ultrasonic velocity determinations in the ternary system $Et_3N–H_2O–Et_4NCl$ were made using the sing around method. Isentropic compressibility values were calculated for different solutions using the Newton–Laplace equation. Excess molar compressions were derived, and least square fitted to Redlich–Kister equations of only one parameter. Negative limiting partial molar isentropic compressions of Et_3N were obtained appearing to indicate that the solvent, surrounding the Et_3N molecule, would present greater resistance to compression than in the bulk.

Limiting partial molar compressions were obtained by adding the molar compression of pure Et_3N to the c parameter of the Redlich–Kister equation. These values are all negative, increasing with temperature and salt concentration. This might signify that both factors work against the promotion of the water structure around Et_3N when it is introduced in pure water due to its hydrophobicity.

Comparison of these results with limiting partial molar volumes and expansions obtained from density data show that while the addition of the salt leads to decreasing values of $V^{\infty}_{\mathrm{Et_3N}}$, the effect on $K^{\infty}_{S,\mathrm{Et_3N}}$ is opposite. The increase of the packing efficiency of the amine as long as the structure of the water becomes more open due to the hydrophobicity of the tetraalkylammonium cation and the progressive cosphere overlapping of this cation and of the amine may be the explanation of these results.

Apparent molar isentropic compressions of Et_3N were also derived point to point from each experimental excess molar value for all the solvents studied. A constancy of the values throughout the amine concentration for all the solvents and temperatures studied points out to a stabilisation of the water structure produced either by the Et_3N molecule in pure water or by the tetraalkylammonium cation in the other solvents.

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