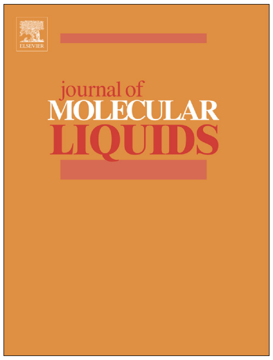

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Thermodynamic Studies of Aqueous Solutions of Ammonium Based Nitrate Protic Ionic Liquids at Different Temperatures (288.15 K to 303.15 K) and 101.325 kPa: A Volumetric Approach

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Abstract: We report the synthesis of two protic ionic liquids (PILs) through atom–economic neutralization reaction between alkylamine (diethlyamine (DEA) and triethylamine (TEA)) and nitric acid. The product ionic liquids are characterized by ^{1}H NMR spectra. The density property of aqueous solutions of synthesised PILs, namely, diethylammonium nitrate (DEAN) and triethylammonium nitrate (TEAN) were measured in the concentration range of ~0.01−~0.5 mol·kg^{-1}for the temperature range of 288.15 K to 303.15 K and at 101.325 kPa. The measured densities were used to calculate the apparent molar volume (V_ϕ), partial molar volume of solvent ($\overline{V}_1$) and solute ($\overline{V}_2$) at all studied temperatures. The limiting apparent molar volumes (V_ϕ^0) are reported. The apparent molar expansivity (E_ϕ) of PILs at finite concentrations as well as at infinite dilutions are reported at 293.15 and 298.15 K. It is observed that water structure making effect exhibited by cations is governed by the hydration of the cations, while the overall kosmotropic effect depends upon the basicity and shape factor of the cation concerned. The hydrophobic solute–solute interactions and ion–pair formation may be influencing the deviation parameter (B_V) of Debye–Hückel equation for volumes.These results are discussed.

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Keywords: Protic ionic liquids, Partial molar volume, Isobaric expansivity, Kosmotropic effect.

1. Introduction

Ionic liquids (ILs)are known as organic molten or fused salts that are liquid at low temperatures generally below 373 K[1]. The recent literature is getting surged day by day the reports of ILs as solvent, catalyst and variety of other uses as solubilization of polymers or their use for degradation [1,2]. It is noted that in literature, the properties of ILs or mixtures of ILs with various solvents including water are being reported over the whole concentration range [3–5]. Such data may not yield useful information about ion–ion and ion–solvent interactions at infinitely dilute solution. There is a need of good quality thermodynamic properties data in finite as well as at infinite concentration of ILs especially in water as a solvent. There are few studies which tried to probe for the molecular and ion interactions in dilute concentration range employing volumetric, speed of sound, viscosity and vapor pressure osmometry measurements [6–15].

The protic ionic liquid (PIL) is a well–characterized sub class of ILs which are simpler, cheaper and environment friendly to synthesize designed from the transfer of proton from Brønsted acid to Brønsted base with no by–product formation ($\mathrm{HA} + \mathrm{B} \Leftrightarrow [\mathrm{BH}]^{+} + [\mathrm{A}]^{-}$)

[2,10,11]. The first ionic liquid discovered by Gabriel in 1888 was ethanolammonium nitrate, having melting point of 325−328 K and was besides the first PIL [16]. Another ionic liquid ethylammonium nitrate having melting point 285 K was synthesized and reported in the scientific literature by Walden in 1914 [17], while Mirejovsky and Arnett [18] have reported the synthesis of ethylammonium nitrate which is having all similar properties as that of water except heat capacity. Among the substitutes to presently used solvents, significant attention has been earned by the PILs because of their distinctive and tunable physical and chemical properties [2]. The PILs having distinguished properties such as low vapour pressure, basicity, thermal stability, high ionicity, hydrophobicity, hydrogen bonding, polarity, large chemical window, non–flammability, and so on [1,2,19,]. These properties of PILs can be tuned for desired application by choosing different combinations of anions and cations and that's the reason for describes them as 'designer solvent' [20,21].

Alkylammonium nitrate PILs with the physiognomies of strong solubility, H–bond formation ability, good catalytic and additives properties have invited extensive attention from both academic community and industry [19–29]. Summers and Fowers [28] observed that, the ethylammonium nitrate [EAN]PIL acts as a denatured-reducing agent used for the recovery of reduced-denatured lysozyme which gives 75 % of its activity in the regular renaturation methods. EAN also acts as the preventing agents of the aggregation of lysozyme i.e. acting as an osmolyte [28]. The above observations are important to understand the denaturation of bio-polymer or proteins in water [30,31].

Recently, in our laboratory we have synthesized and characterized the protic ionic liquids (PILs) successfully [10,11].As a continuance of our PILs studies, we report in this communication, the synthesis of two protic ionic liquids namely, diethylammonium nitrate

[DEAN] and triethylammonium nitrate [TEAN] and studies related to their volumetric behaviour in dilute aqueous solutions (~0.01 to ~0.5 mol·kg^{-1}) for the temperature range of 288.15 to 303.15 K and at 101.325 kPa. Using experimental density data, the calculations of parameters like apparent molar volume (V_ϕ), partial molar volume of solvent ($\bar{V}_1$) and solute ($\bar{V}_2$), isobaric expansivity (α) and apparent molar expansivity (E_ϕ), the limiting apparent molar volume (V_ϕ^0) and limiting apparent molar expansivity (E_ϕ^0) were made. The results are presented and discussed.

2. Experimental procedure

2.1 Materials

All chemicals were purchased from different sources which were required for the synthesis of ammonium based nitrate protic ionic liquids. These are listed in Table 1 with mass fraction purity. All were used without further purification.

2.2 Synthesis of protic ionic liquids

Synthesis of PILs namely diethylammonium nitrate [DEAN] and triethylammonium nitrate [TEAN] was carried out in same way using reported methods [22,23]. The DEAN and TEAN are prepared by a simple acid–base reaction: stoichiometric quantity of nitric acid is added into alkylamine (diethlyamine [DEA] and triethylamine [TEA]) respectively. The diethylamine were charged into a three neck round bottom flask equipped with a Nitrogen gas purging and a dropping funnel with the tip under stopcock. Then nitric acid was added drop wise into diethlyamine using dropping funnel. The above mixture in the round bottom flask was kept in an ice cold (273 K) condition with constant stirring as the reaction is highly exothermic. The reaction mixture was stirred at 273 K for 1 h and then at 303K for 4−5 h for completion of reaction. Any traces of reactant was removed by applying high vacuum at 323 K and finally, to obtain pale yellow solid product as DEAN. The same procedure was followed for the synthesis of TEAN which yields white crystals. The melting point of synthesized DEAN and TEAN are 367 K and 385 K, respectively which agree well those reported in literature [22,23].

After drying at appropriate vacuum and temperature conditions, resulting PILs were then stored in dry conditions under phosphorous pentaoxide (P_2O_5) in a desiccator. The structures and purity of the DEAN and TEAN were confirmed by using ^{1}H NMR spectra obtained at 300 MHz Bruker instrument in $CDCl_3$ as a solvent (Supplementary Data, Fig.S1−S2). No any residues of impurities were detected in ^{1}H NMR spectra. The chemical structures of synthesized PILs are schematically represented in Fig. 1. Water contents in the synthesized PILs were determined by Karl–Fischer titration and found to be 0.0025 mass fractions for DEAN and 0.0021 mass fractions for TEAN respectively. These water contents were taken into consideration during preparation of solutions to determine concentrations.

2.3 Preparations of sample solutions

All the solutions of studied PILs were prepared on molality basis at room temperature in the air tight glass vessels and whenever necessary converted to molarity scale using density data. Quartz doubly distilled water was used for the entire work. A SHIMADZU AUW220D balance having readability of 0.01 mg was used for weighing. The standard uncertainties in the molality of solutions were found to be $\pm 5\cdot10^{-5}\text{mol}\cdot\text{kg}^{-1}$.

2.4 Density Measurements

The density measurements were made using DMA–5000 Anton Paar Digital Densitometer at 288.15, 293.15, 298.15 and 303.15±0.01K. The densitometer was calibrated using the air and water at the studied temperatures. After applying the humidity and lab pressure corrections, the uncertainty in the density measurements was found to be $\pm 3\cdot 10^{-3}$ $kg\cdot m^{-3}$. The methodology of density measurements and other details are described earlier [13,14,32]

3. Results

3.1 Density and Apparent Molar Volume

The experimental density (ρ) data for aqueous solutions of DEAN (0.01923 to 0.50456 $mol\cdot kg^{-1}$) and for aqueous solutions of TEAN (0.01991 $mol\cdot kg^{-1}$ and 0.51256 $mol\cdot kg^{-1}$) at different temperatures (288.15, 293.15, 298.15 and 303.15 K) are collected in Table 2 and Table 3, respectively. The variations of ρ data as a function of molality of DEAN and TEAN at all studied temperatures are shown in Fig.S3 and Fig.S4 (Supplementary Data: Fig.S3 and Fig.S4), respectively.

Further, the ρ data were used to calculate the apparent molar volumes (V_ϕ) of both studied PILs in aqueous solutions at finite concentration by using the Eq. (1) [33]

$$V_\phi = \frac{(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M}{\rho} \tag{1}$$

where ρ_0 and ρ are the densities(in $kg\cdot m^{-3}$) of solvent and solution, respectively, m is molality of the solute ($mol\cdot kg^{-1}$) and M is the molar mass of the solute ($kg\cdot mol^{-1}$).

The V_ϕ data of DEAN and TEAN in aqueous solutions along with their uncertainties at studied temperatures are collected in Table 2 and Table 3, respectively.

The V_ϕ data can also be expressed as [33–35],

$$V_\phi = V_\phi^0 + S_V c^{1/2} + B_V c \tag{2}$$

where V_ϕ^0 is apparent molar volume of the solute at infinite dilution, S_V is Debye–Hückel limiting law coefficient (1.697, 1.782, 1.868and 1.955·10^{-6} (mol·mm^{-3})$^{-3/2}$ for 1:1 electrolyte solutions at 288.15, 293.15, 298.15 and 303.15 K, respectively) [32,34,36], c is the concentration of the solute in aqueous solutions (mol·dm^{-3}) and B_V is a deviation parameter (m^6·mol^{-2}).

The variation of $V_\phi - S_V c^{1/2}$ as a function of concentration (c/mol·dm^{-3}) of DEAN and TEAN in aqueous solutions at 288.15, 293.15, 298.15 and 303.15 K are shown in Fig. 2 and Fig. 3, respectively. The limiting apparent molar volume (V_ϕ^0) are obtained by the smooth extrapolation of parameter ($V_\phi - S_V c^{1/2}$)to infinitely dilute solutions and the value of B_V parameters are estimated from the slope of the graph. The values of V_ϕ^0 and B_V for DEAN and TEAN in aqueous solutions at studied temperatures are collected in Table 4.

3.2 Partial Molar Volume

The partial molar volume of solute ($\overline{V}_2$) and partial molar volume of solvent ($\overline{V}_1$) of both studied PILs were calculated from experimental density data using Eqs. (3) and (4) [10,13,33,35]

$$\overline{V}_2 = V_\phi + \left[\frac{1000 - cV_\phi}{2000 + c\sqrt{c}\,\dfrac{dV_\phi}{d\sqrt{c}}}\right]\sqrt{c}\,\frac{dV_\phi}{d\sqrt{c}} \tag{3}$$

$$\overline{V}_1 = \frac{M_1}{\rho - c\left(\dfrac{\partial\rho}{\partial c}\right)} \tag{4}$$

$\overline{V}_2$ and $\overline{V}_1$ data for DEAN and TEAN in aqueous solutions at studied temperatures are incorporated in Table 2 and Table 3, respectively.

3.3 Coefficient of expansion and apparent molar expansivity

The isobaric expansivity coefficient (α) of studied PILs in aqueous solutions at finite concentrations were estimated as [11,37]:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,m} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{P,m} \tag{5}$$

The calculated values of α for the aqueous solutions of DEAN and TEAN at 293.15 and 298.15 K are reported in Table 2 and 3, respectively.

The apparent molar expansivity(E_ϕ) can be obtained at 293.15 and 298.15 K using the Harned and Owen method as [33]:

$$E_\phi = \frac{(\alpha\rho_0 - \alpha_0\rho)}{m\rho\rho_0} + \left(\frac{M\alpha}{\rho}\right) \tag{6}$$

where, α and α_0 are the isobaric expansivity coefficients for solution and solvent, respectively, ρ and ρ_0 are the densities (in kg·m^{-3})of solution and solvent, respectively, and M is the molar mass of the solute (kg·mol^{-1}).

The obtained values of E_ϕ for aqueous solutions of DEAN and TEAN at 293.15 and 298.15 K were collected in Table 2 and 3, respectively.

Further, E_ϕ data can also be expressed as [33]:

$$E_\phi = E_\phi^0 + S_E m \tag{7}$$

where, E_ϕ^0 is the limiting apparent molar expansivity and S_E is the limiting slope.

On plotting the graphs of E_ϕ data (calculated with the help of Eq.(6)) as a function of molality (m/mol·kg^{-1}) of DEAN and TEAN in aqueous solutions at 293.15 and 298.15 K(Figs.4 and 5), the intercept and slope of the lines results into the values of E_{ϕ}^{0} and S_E, respectively, and the data are collected in Table 4.

The limiting apparent molar expansivity (E_{ϕ}^{0}) can also be expressed as [33]:

$$E_{\phi}^{0} = \left(\frac{\partial V_{\phi}^{0}}{\partial T} \right)_{P} = a_1 + 2a_2 \mathrm{T} \tag{8}$$

where, a_1 and a_2 are the differential coefficients, derived on the basis of increase in volume with rise in temperature.

The calculated values of E_{ϕ}^{0} using Eq. (8) for DEAN and TEAN at all studied temperatures are also reported in Table 4.

4. Discussion

The density values of the mixtures increase linearly as a function of molality of studied PILs at all studied temperatures (Table 2 and 3, and Fig. S3 and S4: Supplementary Data). For a given molality of PILs solutions the densities values decrease as the temperature increases. An examination of Tables 2 and 3 and Figs. 2 and 3 indicate that, the V_{ϕ} values vary little in the studied concentration region at all studied temperatures. The parameter ($V_{\phi} - S_V c^{1/2}$) values also exhibit small deviations from the Debye–Hückel limiting law equation as a function of concentration , affecting the deviation parameter (B_V) little, for both studied PILs at all studied temperatures. In our earlier work with imidazolium salts in water with respect to osmotic coefficients of solutions and mean ionic activity coefficients, we noted that in such solutions Debye–Hückel limiting law is approximately obeyed, exhibiting small differences in volume values from Debye–Hückel limiting law equation for volumes [7]. We confirm such a case for the volumetric behaviour for the studied PIL's suggesting similar type of ion-solvent interactions (ionic hydration). It is known that NO_3^- a planer anion is water structure breaker [38], while the hydrophobic cations exhibit negative dependence for volume. Probably there exists a compensation effect for volume of the salts due to both cation–solvent and anion–solvent interactions.

The values of limiting apparent molar volume (V_ϕ^0) increase for both the studied PILs as temperature increases (Table 4), which suggests that, the ion–solvent interactions increases as the temperature increases [11,13]. The V_ϕ^0 values also increase with increasing the alkyl chain length/hydrophobicity of cations for a given homologous series [10,11,37]. B_V is the deviation parameter (Eq. (2)), which is generally negative for water structure making ions (Kosmotropic effect) and positive for water structure breaking ions (Chaotropic effect) [10,11,37,39]. In present study, we observe small negative B_V values for both studied PILs due to hydrophobic hydration effects and Gurney's cosphere overlap effects [40] which mean that, the ions of studied PILs specially cations are water structure making ions at all studied temperatures, except for DEAN at 288.15 K, for which B_V value is small positive in magnitude (Table 4). In fact for small sized (high charge density) 1:1 electrolytes positive B_V values are expected due to predominance of cation-solvent (charge–dipole) interaction effects. This has been nicely elucidated in the discussion on ionic hydration in the book by Harned and Owen [33]. We could observe a small positive B_V value at low temperature (288.15 K0 for DEAN and almost zero value at 293.15 K signifying that ion-solvent interaction effects are significantly affected by charge-density of the cations and temperature. The negative magnitude of B_V values increase at 298.15 K and 303.15 K for DEAN and for TEAN at all studied temperatures, the negative magnitude of B_V values increases with increase in temperature, due to hydrophobic interactions of cation with solvent water/due to solvent enforced ion–pairing (cation–cation interactions) [13] and cosphere overlap effect [40]. These observations demonstrate that hydrophobic interaction effects increase with increase in temperature in accordance with the concept of water structure making hydrophobic hydration of cations (kosmotropic effect).

The individual volumes of the cations have been calculated at 298.15 K as 85.01 and $115.35 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$ for DEAN and TEAN, respectively, by subtracting the anion NO_3^- contribution as $34.30 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$[38] from the V_ϕ^0 values of studied PILs at 298.15 K. The calculation of contribution of increased alkyl groups in TEAN yields the value of $15.17 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$for per methylene group which is in harmony with the results for aqueous solutions of alkanes, alcohols and amines [41]. It is known that NO_3^- anion is a water structure breaking [38,42,43]. Thus the hydration of PILs seem to depend upon both the alkyl group hydration as well on the basicity of N^+ charge centre; along with the nature of anion–solvent interaction. The observed value also can be rationalized on the basis of Hepler's constant [44] values given in Table 4.

We note from the examination of E_ϕ (or E_ϕ^0) values, there exists a differentiation in the mode of interaction of N^+ charge centre and alkyl–chain residues with water. It was seen that for DEAN, the E_ϕ^0 values are similar to those of tetraalkylammonium salts which decrease with increase in temperature while for TEAN: the values are of lesser in magnitude than DEAN and increases slightly. Probably, in DEAN, the alkyl residue–water interactions are stronger, while in case of more symmetric TEAN, the interactions at the N^+ charge centre (charge–dipole) also contribute (in negative direction) with increase in thermal energy. This distinction can be supported on the basicity of aliphatic amines wherein the introduction of an alkyl group into ammonia increases the basic strength initially but the third alkyl group causes a decrease in basicity. This is due to the fact that the basic strength of an amine in water is determined not only by electron availability on the nitrogen atom but also by the extent to which the cation, formed by uptake of a proton, can undergo solvation and so become stabilized. Therefore, our expansivity results nicely reflect the mode and the role of N^+ charge centre in hydration equilibria in case of DEAN and TEAN.

5. Conclusions

We have synthesized the two PIL, namely, diethylammonium nitrate [DEAN] and triethylammonium nitrate [TEAN] and characterised their structure by ^{1}H NMR spectra. Apparent molar volume and partial molar volume for aqueous solutions of DEAN and TEAN as a function of concentration at T = 288.15–303.15K have been reported. It is observed that for both studied PILs, the deviation parameter B_V of Debye–Hückel theory for volumes are negative which means both of them acts as water structure making ions due to the effect of overlap for solvent cosphere. The single ion partial molar volume of cations are calculated and which are equal to 85.01 and $115.35 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$ for DEAN and TEAN, respectively.The increment in volume due to the addition of the methylene group is found to be $15.17 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$. Its seems that, there is a some compensation effect on volume due to water structure stabilizing influences of cations and water–structure breaking effect due to anion-water (NO_3^-–water) interactions. More studies are required in this direction. The apparent molar expansivity parameter provides indirectly information about the charge–dipole interactions as well of the alkyl–groups in cations with surrounding water shell more subtly. Our results thus stress the need of obtaining and examining the expansivity data for aqueous solutions of model protic ionic liquids.

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Captions to the Figures

Fig. 1. Molecular structures of the studied protic ionic liquids.

Fig. 2. Variation of parameter ($V_{\phi} - S_V c^{1/2}$) as a function concentration (c/mol·dm^{-3}) of DEAN in aqueous solution: ●, 288.15 K; ▲, 293.15 K; ■, 298.15 K; ♦, 303.15 K.

Fig. 3. Variation of parameter ($V_{\phi} - S_V c^{1/2}$) as a function concentration (c/mol·dm^{-3}) of TEAN in aqueous solution: ●, 288.15 K; ▲, 293.15 K; ■, 298.15 K; ♦, 303.15 K.

Fig. 4. Variation of apparent molar expansivity (E_{ϕ})as a function molality (m)of DEAN in aqueous solution at ▲, 293.15 K; ■, 298.15 K.

Fig. 5. Variation of apparent molar expansivity (E_{ϕ})as a function molality (m)of TEAN in aqueous solution at ▲, 293.15 K; ■, 298.15 K.

Captions to the Tables

Table 1 List of chemical name, CAS number, molecular mass, purity and source of chemicals used.

Table 2 Molality (m), density (ρ), apparent molar volume (V_ϕ),$V_\phi - S_V c^{1/2}$, partial molar volume of solute ($\overline{V}_2$), partial molar volume of solvent ($\overline{V}_1$) and isobaric expansivity (α) data for aqueous solutions of DEAN at 288.15, 293.15, 298.15, and 303.15 K and apparent molar expansivity (E_ϕ) at 293.15 and 298.15 K and at ambient pressure of 101.325 kPa.^{a}

Table 3 Molality (m), density (ρ), apparent molar volume (V_ϕ),$V_\phi - S_V c^{1/2}$, partial molar volume of solute ($\overline{V}_2$), partial molar volume of solvent ($\overline{V}_1$) and isobaric expansivity (α) data for aqueous solutions of TEAN at 288.15, 293.15, 298.15, and 303.15 Kand apparent molar expansivity ( ) at 293.15 and 298.15 K and at ambient pressure of 101.325 kPa.^{a}

Table 4 Limiting apparent molar volume (V_ϕ^0), deviation parameter (B_V), limiting apparent molar expansivity (E_ϕ^0), limiting slope and Hepler's constant ($\left(\partial^2 V_\phi^0 / \partial T^2\right)_P$)data for aqueous solutions of PILs at different temperatures and at ambient pressure of 101.325 kPa.^{a}

Table 1

Chemical name	CAS No.	Molecular mass ($kg \cdot mol^{-1}$)	Water Content (mass fraction)	Mass fraction purity	Source
Diethlyamine	109–89–7	0.07314		$\geq 0.99^{a}$	Merck
Triethylamine	121–44–8	0.10119		$\geq 0.99^{a}$	Merck
Nitric acid	7697–32–2	0.06301		$> 0.70^{a}$	Merck
Phosphorus pentaoxide	1314–56–3	0.14195		$\geq 0.98^{a}$	Merck
DEAN[b]	27096–30–6	0.13616	0.0025	$\geq 0.99^{c}$	Synthesized in lab
TEAN[b]	27096–31–7	0.16420	0.0021	$\geq 0.99^{c}$	Synthesized in lab

[a] Used as received without purification.

[b] All the PILs used here are synthesized (see section 2.2 below). Diethylammoniumnitrate [DEAN], triethylammonium nitrate [TEAN].

[c] Dried at 343.15 K for 3 days under vacuum in presence of P_2O_5. The synthesized PIL was dried by applying high vacuum at 323.15 to 328.15 K. The purity was checked by ^{1}H NMR spectroscopic techniques.

Table 2

m^a /mol·kg^{-1}	ρ^a /kg·m^{-3}	$10^6 \cdot V_\phi$ /m^3·mol^{-1}	$10^6 \cdot (V_\phi - S_V c^{1/2})$ /m^3·mol^{-1}	$10^6 \cdot \overline{V}_2$ /m^3·mol^{-1}	$10^6 \cdot \overline{V}_1$ /m^3·mol^{-1}	$10^4 \cdot \alpha$ /K^{-1}	$10^6 \phi_E$ /m^3·mol^{-1}·K^{-1}
			***T* = 288.15 K**				
0.00000	999.104		116.61**		18.031		
0.01923	999.483	116.50±0.16	116.26	116.67±0.16	18.031		
0.03884	999.863	116.62±0.08	116.28	116.85± 0.08	18.030		
0.06450	1000.335	117.02±0.05	116.59	117.32± 0.05	18.030		
0.07676	1000.559	117.12±0.04	116.65	117.45± 0.04	18.030		
0.09792	1000.910	117.59±0.03	117.06	117.97± 0.03	18.031		
0.13369	1001.588	117.38±0.02	116.76	117.81± 0.02	18.030		
0.16666	1002.142	117.66±0.02	116.98	118.14± 0.02	18.031		
0.19534	1002.664	117.61±0.02	116.86	118.13± 0.01	18.030		
0.24617	1003.507	117.84±0.01	117.02	118.42± 0.01	18.031		
0.29638	1004.398	117.76±0.01	116.86	118.39± 0.01	18.031		
0.34611	1005.240	117.80±0.01	116.82	118.47± 0.01	18.031		
0.39778	1006.087	117.87±0.01	116.83	118.59± 0.01	18.032		
0.44806	1006.921	117.88±0.01	116.78	118.64± 0.01	18.032		
0.50456	1007.856	117.87±0.01	116.70	118.66± 0.01	18.032		
			***T* = 293.15 K**				
0.00000	998.204		117.72**		18.047	2.061	
0.01923	998.567	117.42±0.16	117.17	117.53± 0.16	18.047	2.110	0.2775
0.03884	998.894	118.49±0.08	118.14	118.65± 0.08	18.047	2.199	0.3823
0.06450	999.314	119.00±0.05	118.55	119.20± 0.05	18.048	2.234	0.2946
0.07676	999.630	117.59±0.04	117.10	117.81± 0.04	18.046	2.175	0.1749
0.09792	999.973	118.06±0.03	117.51	118.31± 0.03	18.046	2.196	0.1641
0.13369	1000.576	118.32±0.02	117.67	118.61± 0.02	18.047	2.291	0.1993
0.16666	1001.118	118.51±0.02	117.79	118.83± 0.02	18.047	2.297	0.1691
0.19534	1001.620	118.45±0.02	117.67	118.79± 0.01	18.047	2.458	0.2326
0.24617	1002.478	118.47±0.01	117.60	118.86± 0.01	18.047	2.368	0.1530
0.29638	1003.303	118.53±0.01	117.58	118.95± 0.01	18.047	2.584	0.2075
0.34611	1004.027	118.83±0.01	117.80	119.27± 0.01	18.048	2.545	0.1704
0.39778	1004.906	118.70±0.01	117.60	119.17± 0.01	18.048	2.588	0.1635
0.44806	1005.601	118.96±0.01	117.79	119.46± 0.01	18.049	2.693	0.1732
0.50456	1006.634	118.64±0.01	117.41	119.16± 0.01	18.047	2.675	0.1536
			***T* = 298.15 K**				
0.00000	997.045		119.41**		18.068	2.566	
0.01923	997.368	119.63±0.16	119.37	119.60± 0.16	18.068	2.594	0.1794
0.03884	997.661	120.54±0.08	120.17	120.49± 0.08	18.069	2.678	0.3217
0.06450	998.106	119.89±0.05	119.42	119.83± 0.05	18.069	2.641	0.1485
0.07676	998.366	119.09±0.04	118.58	119.04± 0.04	18.068	2.665	0.1612
0.09792	998.699	119.37±0.03	118.79	119.31± 0.03	18.068	2.724	0.1940

0.13369	999.283	119.46±0.02	118.78	119.38± 0.02	18.068	2.727	0.1535
0.16666	999.835	119.39±0.02	118.64	119.31± 0.02	18.068	2.744	0.1400
0.19534	1000.146	120.22±0.02	119.41	120.13± 0.02	18.071	2.758	0.1320
0.24617	1001.107	119.48±0.01	118.57	119.38± 0.01	18.068	2.795	0.1267
0.29638	1001.743	120.05±0.01	119.05	119.94± 0.01	18.071	2.895	0.1460
0.34611	1002.680	119.51±0.01	118.44	119.39± 0.01	18.068	2.771	0.0926
0.39778	1003.465	119.56±0.01	118.41	119.43± 0.01	18.068	2.902	0.1195
0.44806	1004.224	119.59±0.01	118.37	119.45± 0.01	18.068	2.915	0.1131
0.50456	1005.139	119.46±0.01	118.17	119.32± 0.01	18.067	2.978	0.1175
T = 303.15 K							
0.00000	995.644		119.90**		18.094		
0.01923	995.971	119.57±0.16	119.30	119.51± 0.16	18.094		
0.03884	996.217	121.80±0.08	121.42	121.72± 0.08	18.095		
0.06450	996.681	120.41±0.05	119.92	120.30± 0.05	18.094		
0.07676	996.951	119.42±0.04	118.88	119.31± 0.04	18.093		
0.09792	997.238	120.14±0.03	119.53	120.01± 0.03	18.094		
0.13369	997.838	119.94±0.02	119.23	119.78± 0.02	18.094		
0.16666	998.367	119.95±0.02	119.16	119.78± 0.02	18.094		
0.19534	998.805	120.05±0.02	119.20	119.87± 0.02	18.094		
0.24617	999.654	119.84±0.01	118.89	119.64± 0.01	18.093		
0.29638	1000.341	120.20±0.01	119.16	119.98±0.01	18.095		
0.34611	1001.244	119.76±0.01	118.64	119.52± 0.01	18.093		
0.39778	1001.973	119.94±0.01	118.74	119.69± 0.01	18.094		
0.44806	1002.684	120.06±0.01	118.78	119.79± 0.01	18.095		
0.50456	1003.616	119.86±0.01	118.51	119.58± 0.01	18.093		

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.3kPa, $u(m)$ = $5\cdot10^{-5}$ mol·kg^{-1}. The combined uncertainties $u_c(\rho) = 3\cdot10^{-3}$ kg·m^{-3}, $u_c(\overline{V}_1) = 2\cdot10^{-9}$ m^3·mol^{-1}, $u_c(\alpha) = 3\cdot10^{-7}$ K^{-1} and $u_c(\phi_E) = 2\cdot10^{-9}$ m^3·mol^{-1}·K^{-1}.

** Extrapolated value at infinitely dilute solution of IL's in water at 288.15, 293.15, 298.15 and 303.15 K.

Table 3

m^a /mol·kg^{-1}	ρ^a /kg·m^{-3}	$10^6\cdot V_\phi$ /m^3·mol^{-1}	$10^6\cdot(V_\phi - S_V c^{1/2})$ /m^3·mol^{-1}	$10^6\cdot\bar{V}_2$ /m^3·mol^{-1}	$10^6\cdot\bar{V}_1$ /m^3·mol^{-1}	$10^4\cdot\alpha$ /K^{-1}	$10^6\phi_E$ /m^3·mol^{-1}·K^{-1}
			***T* = 288.15 K**				
0.00000	999.104		148.19^{**}		18.031		
0.01991	999.422	148.30±0.15	148.06	148.38± 0.015	18.031		
0.03720	999.691	148.45±0.08	148.13	148.55± 0.08	18.031		
0.05696	999.995	148.54±0.05	148.14	148.67± 0.05	18.031		
0.07729	1000.305	148.60±0.04	148.13	148.75± 0.04	18.031		
0.09748	1000.605	148.70±0.03	148.17	148.86± 0.03	18.031		
0.12802	1001.061	148.74±0.02	148.14	148.93± 0.02	18.031		
0.16978	1001.678	148.78±0.02	148.09	148.99± 0.02	18.031		
0.19761	1002.078	148.83±0.02	148.08	149.05± 0.02	18.031		
0.25390	1002.890	148.84±0.01	148.01	149.10± 0.01	18.031		
0.29805	1003.510	148.88±0.01	147.98	149.15± 0.01	18.031		
0.35177	1004.258	148.90±0.01	147.92	149.19± 0.01	18.031		
0.39754	1004.876	148.94±0.01	147.90	149.25± 0.01	18.031		
0.45221	1005.629	148.92±0.01	147.82	149.24± 0.01	18.031		
0.51256	1006.430	148.94±0.01	147.77	149.28± 0.01	18.031		
			***T* = 293.15 K**				
0.00000	998.204		149.11^{**}		18.047	2.061	
0.01991	998.505	149.28±0.15	149.03	149.33± 0.015	18.047	2.090	0.1762
0.03720	998.761	149.39±0.08	149.04	149.46± 0.08	18.047	2.111	0.1670
0.05696	999.050	149.46±0.05	149.04	149.55± 0.05	18.047	2.136	0.1641
0.07729	999.346	149.50±0.04	149.00	149.60± 0.04	18.047	2.161	0.1615
0.09748	999.636	149.54±0.03	148.99	149.65± 0.03	18.047	2.181	0.1565
0.12802	1000.066	149.62±0.02	148.99	149.75± 0.03	18.047	2.219	0.1566
0.16978	1000.650	149.67±0.02	148.95	149.82± 0.02	18.047	2.272	0.1587
0.19761	1001.035	149.69±0.02	148.91	149.86± 0.01	18.047	2.298	0.1548
0.25390	1001.812	149.69±0.01	148.81	149.87± 0.01	18.047	2.366	0.1557
0.29805	1002.400	149.74±0.01	148.79	149.93± 0.01	18.048	2.406	0.1519
0.35177	1003.130	149.70±0.01	148.67	149.91± 0.01	18.047	2.460	0.1506
0.39754	1003.730	149.72±0.01	148.63	149.94± 0.01	18.047	2.512	0.1512
0.45221	1004.450	149.70±0.01	148.54	149.93± 0.01	18.047	2.584	0.1545
0.51256	1005.194	149.76±0.01	148.53	150.00± 0.01	18.048	2.637	0.1520
			***T* = 298.15 K**				
0.00000	997.045		149.75^{**}		18.068	2.566	
0.01991	997.335	149.99±0.15	149.73	150.05± 0.15	18.068	2.597	0.1938
0.03720	997.583	150.06±0.08	149.70	150.13± 0.08	18.068	2.618	0.1799
0.05696	997.862	150.14±0.05	149.69	150.23± 0.05	18.068	2.637	0.1643
0.07729	998.148	150.17±0.04	149.65	150.27± 0.04	18.068	2.665	0.1689

0.09748	998.426	150.23±0.03	149.65	150.35± 0.03	18.068	2.684	0.1618
0.12802	998.847	150.26±0.02	149.59	150.39± 0.02	18.068	2.719	0.1608
0.16978	999.411	150.31±0.02	149.55	150.47± 0.02	18.068	2.765	0.1594
0.19761	999.784	150.33±0.02	149.51	150.50± 0.02	18.068	2.785	0.1533
0.25390	1000.528	150.36±0.01	149.44	150.55± 0.01	18.068	2.862	0.1598
0.29805	1001.111	150.35±0.01	149.35	150.55± 0.01	18.068	2.891	0.1530
0.35177	1001.797	150.38±0.01	149.30	150.60± 0.01	18.068	2.944	0.1520
0.39754	1002.360	150.44±0.01	149.29	150.66± 0.01	18.069	3.013	0.1581
0.45221	1003.035	150.46±0.01	149.24	150.70± 0.01	18.069	3.071	0.1582
0.51256	1003.791	150.43±0.01	149.14	150.68± 0.01	18.069	3.088	0.1486
***T* = 303.15 K**							
0.00000	995.644		150.76**		18.094		
0.01991	995.915	151.15±0.15	150.87	151.17± 0.15	18.094		
0.03720	996.150	151.12±0.08	150.75	151.15± 0.08	18.094		
0.05696	996.420	151.06±0.05	150.59	151.09± 0.05	18.094		
0.07729	996.688	151.13±0.04	150.60	151.17± 0.04	18.094		
0.09748	996.958	151.12±0.03	150.52	151.17± 0.03	18.094		
0.12802	997.355	151.18±0.02	150.48	151.23± 0.02	18.094		
0.16978	997.893	151.21±0.02	150.42	151.27± 0.02	18.094		
0.19761	998.257	151.18±0.02	150.33	151.25± 0.02	18.094		
0.25390	998.957	151.25±0.01	150.29	151.32± 0.01	18.094		
0.29805	999.518	151.22±0.01	150.18	151.29± 0.01	18.094		
0.35177	1000.188	151.20±0.01	150.07	151.28± 0.01	18.094		
0.39754	1000.715	151.28±0.01	150.09	151.37± 0.01	18.094		
0.45221	1001.371	151.27±0.01	150.00	151.36± 0.01	18.094		
0.51256	1002.106	151.22±0.01	149.87	151.31± 0.01	18.094		

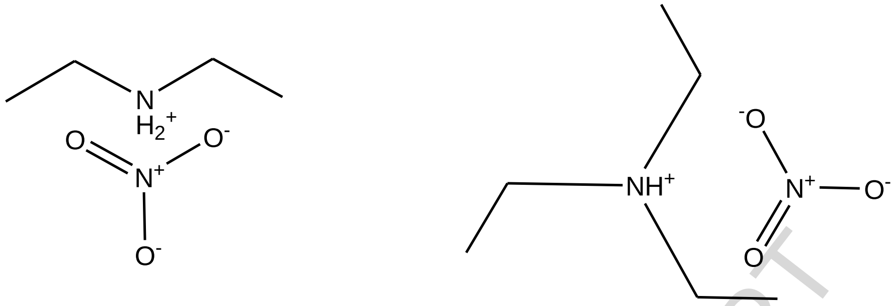
[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.3 kPa, $u(m)$ = $5 \cdot 10^{-5}$ mol·kg^{-1}. The combined uncertainties $u_c(\rho) = 3 \cdot 10^{-3}$ kg·m^{-3}, $u_c(\overline{V}_1) = 2 \cdot 10^{-9}$ m^3·mol^{-1}, $u_c(\alpha) = 3 \cdot 10^{-7}$ K^{-1} and $u_c(\phi_E) = 2 \cdot 10^{-9}$ m^3·mol^{-1}·K^{-1}.

** Extrapolated value at infinitely dilute solution of IL's in water at 288.15, 293.15, 298.15 and 303.15 K.

Table 4

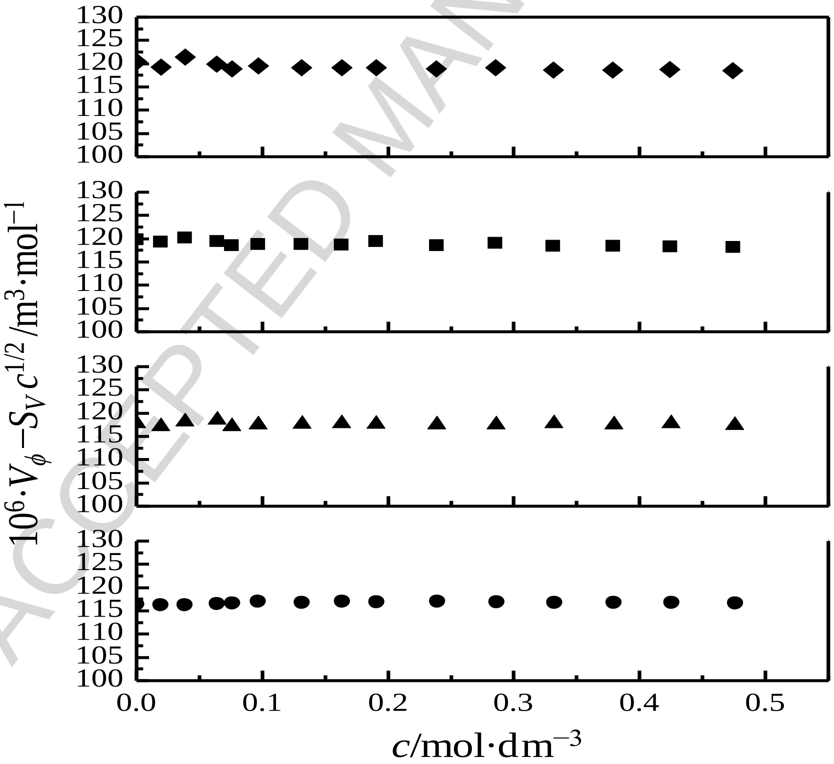
T/ K	$10^6\cdot V_\phi^0$ / $m^3\cdot mol^{-1}$	$10^6\cdot B_V$ / $m^6\cdot mol^{-2}$	$10^6\cdot E_\phi^0$ /$m^3\cdot mol^{-1}\cdot K^{-1}$ (Eq. (8))	$10^6\cdot E_\phi^0$ /$m^3\cdot mol^{-1}\cdot K^{-1}$ (Eq. (7))	$10^6\cdot S_E$ / $m^6\cdot mol^{-2}\cdot K^{-1}$	$\left(\partial^2 V_\phi^0 / \partial T^2\right)_P$ /$m^3\cdot mol^{-1}\cdot K^{-2}$
			DEAN			$-1.24\cdot 10^{-2}$
288.15	116.61 ± 0.10	0.65 ± 0.42	0.324 ± 0.0003			
293.15	117.72 ± 0.17	−0.25 ± 0.70	0.262± 0.0004	0.263 ± 0.025	−0.25 ± 0.09	
298.15	119.41 ± 0.19	−2.60 ± 0.74	0.200± 0.0003	0.202 ± 0.020	−0.22 ± 0.07	
303.15	119.90 ± 0.27	−3.18 ± 1.06	0.138± 0.0003			
			TEAN			$0.18\cdot 10^{-2}$
288.15	148.19 ± 0.02	−0.81 ± 0.08	0.154 ± 0.0001			
293.15	149.11 ± 0.02	−1.24 ± 0.06	0.163 ± 0.0001	0.165 ± 0.002	−0.03 ± 0.008	
298.15	149.75 ± 0.01	−1.28 ± 0.03	0.172 ± 0.0001	0.174 ± 0.003	−0.05 ± 0.014	
303.15	150.76 ± 0.03	−1.92 ± 0.12	0.181± 0.0002			

[a] Standard uncertainties $\underline{u}$ are $u(T)$ = 0.01 K, $u(p)$ = 0.3kPa.



Diethylammonium Nitrate
Triethylammonium Nitrate

Fig. 1.



130
125
120
115
110
105
100
$10^6 \cdot V_\phi - S_V c^{1/2}$ /m^3·mol^{-1}
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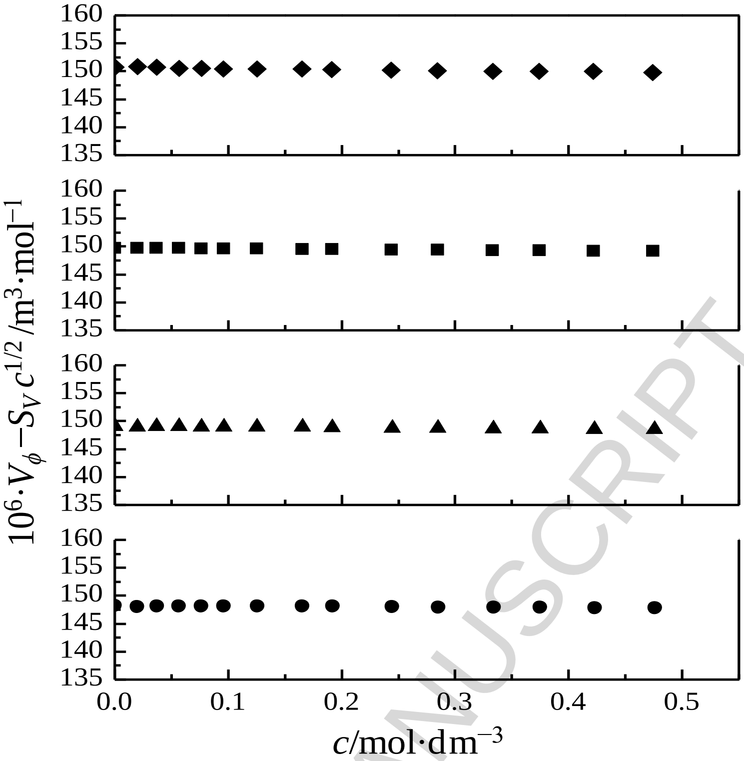
0.1
0.2
0.3
0.4
0.5
c/mol·dm^{-3}

Fig. 2.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155
150
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140
135
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0.1
0.2
0.3
0.4
0.5
c/mol·dm^{-3}

Fig. 3.

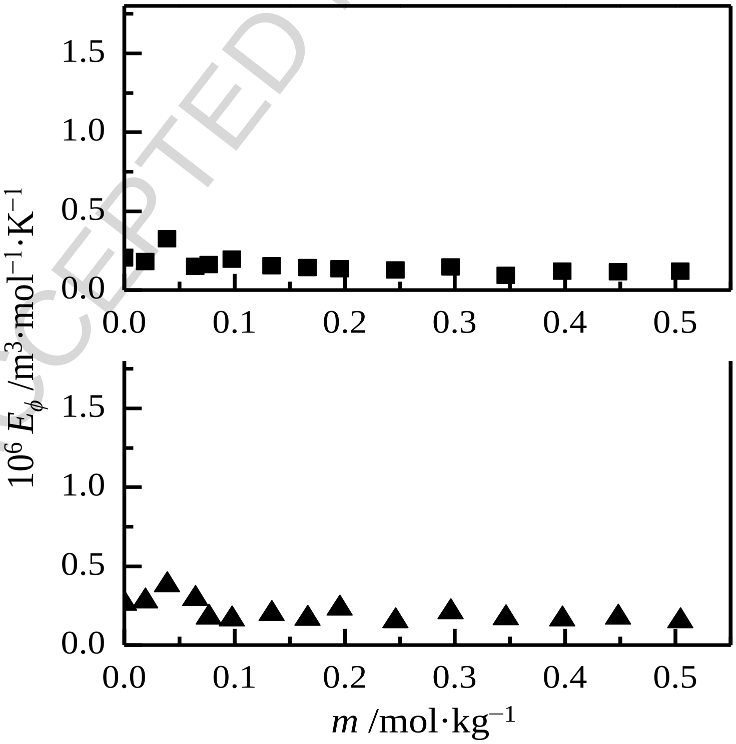
1.5
1.0
0.5
0.0
$10^6 E_\phi$ /m^3·mol^{-1}·K^{-1}
0.0
0.1
0.2
0.3
0.4
0.5
m /mol·kg^{-1}

Fig. 4.

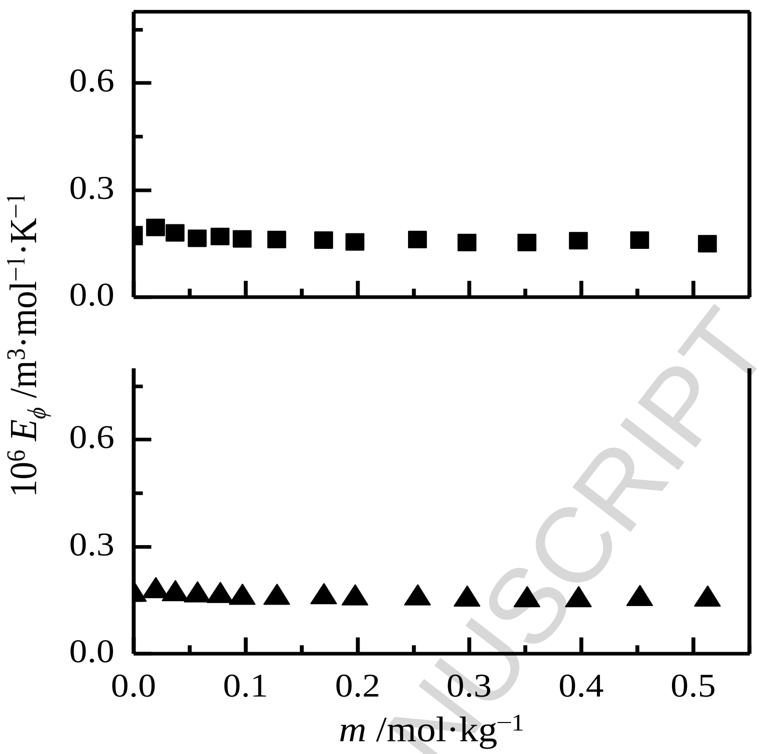

Fig. 5.

Graphical Abstract:

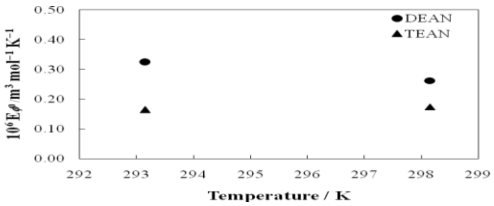

Figure: Variation of limiting apparent molar expansivity (E_ϕ^0) as a function of temperature for diethylammonium nitrate (DEAN) and triethylammonium nitrate (TEAN).

Highlights:

- Synthesis and characterization of protic ionic liquids (PILs).
- Densities of PILs in aqueous solutions are measured at T = 288.15–303.15 K.
- Apparent and partial molar volume of PILs as solute are calculated.
- Isobaric expansivity and apparent molar expansivity of PILs are also obtained.
- The individual volumes of the cations have been calculated at 298.15 K.