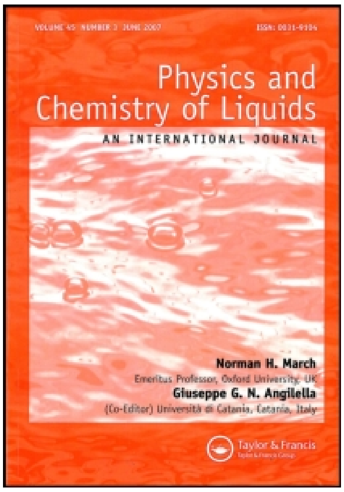

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Density and refractive index in binary mixtures of triethylamine-water in the temperature interval (283.15-291.35) K

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Density and refractive index in binary mixtures of triethylamine–water in the temperature interval (283.15–291.35) K

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Densities ρ, refractive indices n, excess molar volumes V^E, refractive index deviations Δn, molar refractions R_m and excess molar refractions ΔR_m were determined over the full range of compositions for the triethylamine–water binary mixture. The experimental measurements of these properties were carried out at atmospheric pressure and temperatures ranging from 283.15 to 291.35 K. The excess molar volumes V^E, excess molar refractions ΔR_m and refractive index deviations Δn have been fitted to the fourth-order Redlich–Kister polynomial equation. These quantities have been discussed in terms of intermolecular interactions between the compounds of the mixtures. Refractive indices were compared with those predicted using several mixing rules.

Keywords: refractive index; density; excess molar volume; triethylamine; water; excess molar refraction; molecular interactions

1. Introduction

Knowledge of the physicochemical and thermodynamic properties of binary liquid mixtures formed by one or two components associated through hydrogen bonds is important from both theoretical and process design aspects. Excess thermodynamic properties, which depend on the composition and/or temperature, are of great importance for the characterisation of the interaction between components.

In our laboratory and as a part of our systematic studies on the thermodynamic and transport properties of liquid mixture, in previous papers [1–4], measurements of refractive index, density, viscosity and heat capacity, and related excess functions for the binary mixture of isobutyric acid + water (*I–W*) have been reported. As an extension of our studies, we are interested in the binary fluid of triethylamine–water (*TEA–W*). In contrast to the (*I–W*) system, the *TEA–W* mixture is known as a typical, partly miscible, system that has a lower critical solution temperature (LCST) [5]. The LCST and the critical concentration of triethylamine (TEA) are $T_c = 18.4^\circ\mathrm{C}$ (291.55 K) and $C_c = 32.1$ wt%, respectively [6]. It is widely believed that the hydration, which is a kind of hydrogen bond readily destroyed by heat, plays a prominent role in this phase behaviour. Moreover, trialkylamines are industrially important liquids, which are used as intermediates in the

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production of polymers such as phenolic resins, corrosion inhibitors, agrochemicals, lubricating additives, pharmaceuticals, textile dyes, paints and polyurethane foams [7]. To the best of our knowledge, no volumetric studies on the *TEA–W* mixture at different temperatures are available. This prompted us to carry out the experimental values of density and the refractive index of *TEA–W* system over the entire range of composition from 283.15 to 291.35 K (very close to *TEA–W* critical temperature, which was identified visually in our laboratory as $T_c = 291.426$ K and at which the critical opalescence was well developed). From these data, excess molar volume, V^E, deviations in refractive index, Δn, molar refraction, R_m, and excess molar refraction, ΔR_m, based on the Lorentz–Lorenz relation, have been computed. These results have been fitted to the Redlich–Kister polynomial equation [8] to derive binary coefficients and estimate the SEs between experimental and calculated results. Calculated values are used to understand the nature of molecular interactions between the mixing components. We have also used several common mixing rules: Lorentz–Lorenz [9,10], Gladstone–Dale [11], Laplace [12], Eykman [13], Arago–Biot [14] and Oster [15] equations to predict refractive index of the mixtures from their respective experimental densities, refractive index and densities of the pure component.

2. Experimental

The TEA was purchased from Prolabo and used without further purification. The water, used in this study, was obtained from deionised and triply distilled operations, and has a specific conductivity of about $10^{-6}\,\Omega^{-1}\,\text{cm}^{-1}$.

All mixtures were prepared from weighed amounts of the pure components. The weight is obtained with a resolution of 10^{-3} g. Some care was taken to avoid moisture and dust in the final sample: namely, baking the syringes and the cells overnight under vacuum and preparing the mixtures in a dust-free area. The cell, in which TEA and water were mixed together, was immersed in a thermally stabilised water bath with thermal regulation in the order of 10^{-3} K over hours. The temperature was measured by using a quartz thermometer (HP 2804 A) giving a resolution of 10^{-3} K, and which was calibrated on an absolute scale within 0.01 K.

Excess volumes, V^E, have been determined from densities measured with an Anton Paar digital precision densimeter (model DMA46), which was modified in our laboratory by controlling temperature with an accuracy of $\pm 10^{-2}$ K through a computer processor using a graphical interface. The density ρ ($\text{g}\,\text{cm}^{-3}$) of a solution was calculated from the electronically measured frequency of a mechanical oscillator filled with the fluid. The filling was operated by means of medical syringes. The oscillator was a U-shaped glass tubing (volume of $0.7\,\text{cm}^3$) placed in a metal block. This apparatus needs to be carefully calibrated with two liquids of different densities; we chose as standards both water, with density data from Physikalish–Technische Bundesanstalt [16], and methanol, with density data from Brunel and Van Bibber [17]. The response time of the apparatus to temperature changes is much higher than the time needed to reach a stable signal. In order to avoid systematic errors when measuring densities of pure liquids at different temperatures, each temperature change was followed by a waiting time of 2 h. The precision of density measurements was $\pm 10^{-4}\,\text{g}\,\text{cm}^{-3}$ and the accuracy for V^E is lower than $2 \times 10^{-3}\,\text{cm}^3\,\text{mol}^{-1}$.

Refractive indices of the pure liquids and solutions were measured in the temperature interval of 283.15–291.35 K using a thermostated digital Abbe refractometer

(Atago, 3T, Tokyo, Japan) at the wavelength of the D-line of sodium, 589.3 nm, and under atmospheric pressure. Temperature was controlled by circulating water into the refractometer through a thermostatically controlled bath with the digital temperature control unit in order to maintain the desired temperature within ±0.01 K. A check of the calibration was performed by comparing the refractive index of isobutyric acid with the existing data [16], which were extrapolated at the same temperature and wavelength. The remaining discrepancies amounted to a few 10^{-4} and were of the order of the scatter of the data as reported by different authors. The sample was injected into the prism assembly by means of an airtight syringe. Refractive index values were measured to an accuracy of ±0.0001 after the sample mixture was thermostatically at equilibrium. In order to obtain consistent values, we held the temperature constant throughout each set of measurements and repeated every experiment three times under the same conditions.

It is worth noting that the TEA is known as an aggressive substance for glass at higher concentrations, since it is considered as a strong base. The evidence of the aggressive effect is revealed by the appearance of a pale yellow colour in the mixture. However, this yellow colour appears only during several days. Thus, it is very important to us to make our measurements during a short period of time. Consequently, all the samples we made showed no colour changes and all glass cells are stable without corrosion effect.

3. Results and discussion

(a) Excess molar volume and refractive index deviation

From refractive indices and densities measurements, refractive index deviations, Δn, defined on a volume fraction basis [18,19], and excess volumes, V^E, have been calculated as:

$$\Delta n = n - \phi_1 n_1 - \phi_2 n_2, \tag{1}$$

$$V^E = x_1 M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right), \tag{2}$$

where n is the refractive index of the mixture, ϕ_i and n_i are the volume fraction associated to the unmixed state and the refractive index of component i, respectively, ρ is the density of the mixture, x_i, M_i and ρ_i are the mole fraction, the molar mass and the density of component i, respectively.

The experimental densities, ρ, refractive index, n, as well as the calculated refractive index deviations Δn and excess volume V^E for the mixture $TEA-W$, including those of pure components, over the entire composition range (and expressed by TEA molar fraction) are presented in Table 1 at different temperatures near and far away from the critical temperature: 291.35, 291.15, 290.15, 288.15, 286.15 and 283.15 K, where $T_c = 291.426$ K. V^E and Δn are shown graphically in Figures 1 and 2. Each set of the experimental results for all systems was fitted by the method of least squares, with all points weighed equally to the Redlich–Kister polynomial equation [8]:

$$\mathrm{Y} = y_1(1 - y_1)\sum_{i=0}^{j} A_i(2y_1 - 1)^i, \tag{3}$$

Table 1. Refractive index, n, densities, ρ, refractive index deviations, Δn, excess molar volume, V^E, and excess molar refractions, ΔR_m, for the mixture *TEA-W* at 283.15, 286.15, 288.15, 290.15, 291.15 and 291.35 K.

x_1	ϕ_1	n	ρ (g cm^{-3})	Δn	V^E (cm^3 mol^{-1})	ΔR_m (cm^3 mol^{-1})
TEA-W at 283.15 K						
0.000	0.0000	1.3336	0.9995	0.0000	0.000	0.0000
0.019	0.1309	1.3459	0.9853	0.0023	−0.416	−0.0060
0.042	0.2532	1.3573	0.9658	0.0043	−0.788	−0.0111
0.077	0.3907	1.3702	0.9362	0.0067	−1.171	−0.0151
0.106	0.4748	1.3778	0.9190	0.0079	−1.498	−0.0198
0.151	0.5756	1.3862	0.8951	0.0086	−1.915	−0.0263
0.211	0.6704	1.3937	0.8680	0.0089	−2.259	−0.0311
0.293	0.7599	1.3998	0.8395	0.0081	−2.558	−0.0361
0.416	0.8443	1.4040	0.8093	0.0059	−2.721	−0.0419
0.615	0.9243	1.4070	0.7750	0.0028	−2.278	−0.0383
1.000	1.0000	1.4100	0.7370	0.0000	0.000	0.0000
TEA-W at 286.15 K						
0.000	0.0000	1.3334	0.9993	0.0000	0.000	0.0000
0.019	0.1314	1.3458	0.9843	0.0025	−0.412	−0.0056
0.042	0.2538	1.3570	0.9642	0.0046	−0.774	−0.0106
0.077	0.3916	1.3697	0.9340	0.0070	−1.129	−0.0143
0.106	0.4758	1.3772	0.9163	0.0081	−1.449	−0.0189
0.151	0.5765	1.3854	0.8924	0.0088	−1.864	−0.0255
0.211	0.6713	1.3927	0.8653	0.0091	−2.204	−0.0304
0.293	0.7606	1.3987	0.8368	0.0084	−2.496	−0.0354
0.416	0.8448	1.4027	0.8066	0.0061	−2.644	−0.0413
0.615	0.9245	1.4056	0.7723	0.0030	−2.173	−0.0377
1.000	1.0000	1.4082	0.7340	0.0000	0.000	0.0000
TEA-W at 288.15 K						
0.000	0.0000	1.3333	0.9990	0.0000	0.000	0.0000
0.019	0.1317	1.3457	0.9836	0.0027	−0.409	−0.0054
0.042	0.2544	1.3568	0.9628	0.0047	−0.764	−0.0102
0.077	0.3922	1.3693	0.9317	0.0071	−1.101	−0.0136
0.106	0.4764	1.3767	0.9138	0.0083	−1.417	−0.0179
0.151	0.5772	1.3848	0.8899	0.0090	−1.834	−0.0245
0.211	0.6719	1.3921	0.8628	0.0093	−2.176	−0.0291
0.293	0.7611	1.3979	0.8343	0.0085	−2.469	−0.0342
0.416	0.8452	1.4019	0.8041	0.0063	−2.617	−0.0398
0.615	0.9247	1.4047	0.7698	0.0032	−2.139	−0.0358
1.000	1.0000	1.4070	0.7318	0.0000	0.000	0.0000
TEA-W at 290.15 K						
0.000	0.0000	1.3332	0.9987	0.0000	0.000	0.0000
0.019	0.1320	1.3457	0.9828	0.0029	−0.406	−0.0051
0.042	0.2549	1.3567	0.9614	0.0050	−0.751	−0.0096
0.077	0.3928	1.3691	0.9290	0.0074	−1.059	−0.0121
0.106	0.4771	1.3764	0.9109	0.0086	−1.369	−0.0162
0.151	0.5778	1.3844	0.8870	0.0093	−1.784	−0.0226
0.211	0.6724	1.3915	0.8599	0.0095	−2.122	−0.0272
0.293	0.7615	1.3973	0.8314	0.0088	−2.407	−0.0317
0.416	0.8455	1.4011	0.8012	0.0065	−2.541	−0.0370
0.615	0.9249	1.4037	0.7669	0.0034	−2.034	−0.0325
1.000	1.0000	1.4058	0.7298	0.0000	0.000	0.0000

(*continued*)

Table 1. Continued.

x_1	ϕ_1	n	ρ (g cm^{-3})	Δn	V^E (cm^3 mol^{-1})	ΔR_m (cm^3 mol^{-1})
TEA-W at 291.15 K						
0.000	0.0000	1.3331	0.9985	0.0000	0.000	0.0000
0.019	0.1321	1.3456	0.9824	0.0030	−0.404	−0.0050
0.042	0.2551	1.3566	0.9605	0.0051	−0.744	−0.0093
0.077	0.3931	1.3690	0.9275	0.0075	−1.034	−0.0114
0.106	0.4774	1.3761	0.9092	0.0086	−1.339	−0.0156
0.151	0.5781	1.3841	0.8853	0.0093	−1.752	−0.0217
0.211	0.6727	1.3912	0.8582	0.0096	−2.086	−0.0262
0.293	0.7617	1.3967	0.8297	0.0087	−2.366	−0.0310
0.416	0.8457	1.4007	0.7995	0.0066	−2.490	−0.0354
0.615	0.9250	1.4033	0.7652	0.0035	−1.964	−0.0300
1.000	1.0000	1.4052	0.7287	0.0000	0.000	0.0000
TEA-W at 291.35 K						
0.000	0.0000	1.3331	0.9985	0.0000	0.000	0.0000
0.019	0.1322	1.3456	0.9823	0.0030	−0.404	−0.0050
0.042	0.2552	1.3566	0.9604	0.0051	−0.742	−0.0093
0.077	0.3932	1.3689	0.9271	0.0075	−1.029	−0.0113
0.106	0.4775	1.3762	0.9090	0.0087	−1.337	−0.0153
0.151	0.5782	1.3841	0.8851	0.0094	−1.750	−0.0216
0.211	0.6728	1.3911	0.8580	0.0096	−2.085	−0.0261
0.293	0.7618	1.3968	0.8295	0.0089	−2.365	−0.0305
0.416	0.8457	1.4006	0.7993	0.0066	−2.490	−0.0353
0.615	0.9250	1.4032	0.7650	0.0035	−1.964	−0.0299
1.000	1.0000	1.4051	0.7285	0.0000	0.000	0.0000

where Y is matching to Δn or V^E, y_1 denotes the triethylamnie volume fraction for Δn or the corresponding mole fraction for V^E, A_i is the polynomial coefficients, j is the polynomial degree, respectively. The solid lines in Figures 1 and 2 represent the values calculated from the smoothing Equation (3). For none of the systems does the precision warrant the use of more than four parameters. The parameters A_0, A_1, A_2, A_3, and the extremum values of excess molar volume for each of the binary mixtures are shown in Table 2, along with the SDs σ:

$$\sigma = \left[\sum_{i=1}^{N} \frac{(Y_{i,\mathrm{cal}} - Y_{i,\mathrm{exp}})^2}{N-j} \right]^{1/2}, \tag{4}$$

where N is the number of experimental data points and j is the number of parameters.

Furthermore, examination of experimental results displayed in Figures 1 and 2 show that the excess molar volume V^E values are negative over the entire range of composition, and V^E curves are shifted in a regular way with increasing temperature. However, the refractive index deviation values, Δn, are positive. This result is expected since Nakata and Sakurai [20] suggested that the signs of Δn and V^E are opposite if the behaviour of the refractive index is not too non-linear between n_1 and n_2. In our mixtures, this rule is truly satisfied in all cases. The extrema of the curve compositions' dependence were found at ~0.7 volume fraction of TEA (~0.4 TEA mole fraction), the magnitude of which is

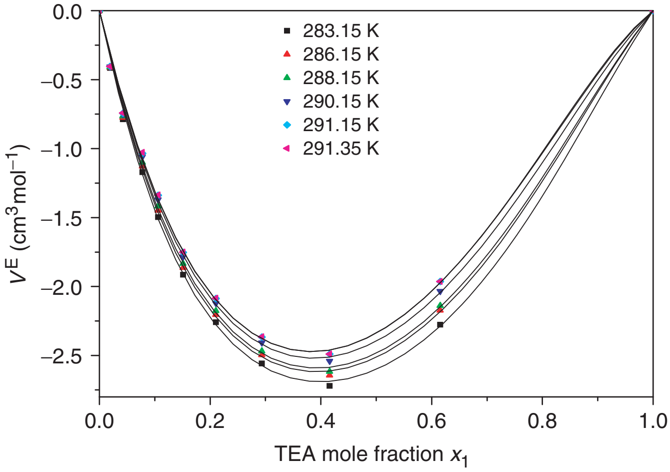

Figure 1. Excess volumes, V^E, for *TEA-W* water mixture at 283.15, 286.15, 288.15, 290.15, 291.15 and 291.35 K as a function of TEA mole fraction x_1 (colour online).
Note: The solid lines represent the values calculated from the smoothing Equation 3.

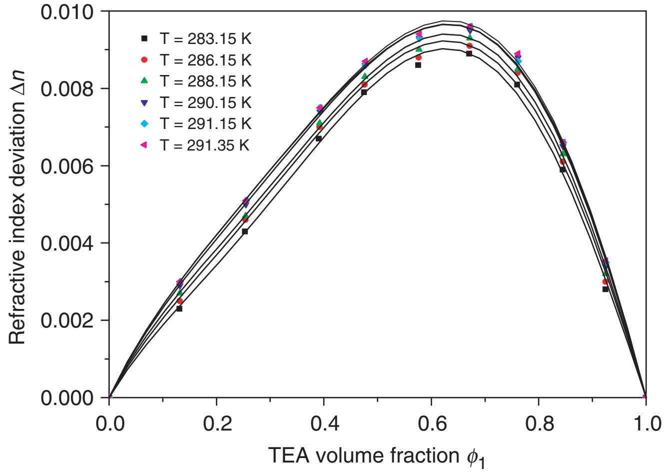

Figure 2. Refractive index deviations, Δn, for *TEA-W* water mixture at 283.15, 286.15, 288.15, 290.15, 291.15 and 291.35 K as a function of TEA volume fraction ϕ_1 (colour online).
Note: The solid lines represent the values calculated from the smoothing Equation 3.

quite large. Moreover, the temperature effect is negative. The negative V^E values indicate that there is a volume contraction on mixing. This result is expected, since the molecular correlations, between water and TEA, are strong. According to Fort and Moore [21], the excess volumes can be interpreted into three terms: namely of physical, chemical and structural effects. The physical effects involve dispersion forces and non-specific interactions in the mixture, adding positive contributions to V^E. The chemical and specific interactions result in a decrease in volume, which includes charge transfer-type forces and other complex-forming interactions between the two species; thereby these

Table 2. Parameters, A_i, and SDs, $\sigma(Y)$, for the Redlich–Kister equation.

	T (K)	A_0 (cm^3 mol^{-1})	A_1 (cm^3 mol^{-1})	A_2 (cm^3 mol^{-1})	A_3 (cm^3 mol^{-1})	σ(Y)
Δn	283.15	0.03276	0.02401	−0.00037	−0.01477	0.0021
	286.15	0.03362	0.02341	0.00180	−0.01313	0.0023
	288.15	0.03417	0.02379	0.00344	−0.01333	0.0017
	290.15	0.03528	0.02327	0.00486	−0.01183	0.0017
	291.15	0.03537	0.02241	0.00599	−0.01032	0.0013
	291.35	0.03562	0.02309	0.00593	−0.01097	0.0015
V^E	283.15	−10.40266	3.50356	−2.08908	3.04703	0.0323
	286.15	−10.05337	3.82044	−1.64522	2.88171	0.0359
	288.15	−9.93434	3.90564	−1.46628	2.61799	0.0384
	290.15	−9.58665	4.22185	−1.01597	2.46634	0.0424
	291.15	−9.35577	4.43403	−0.67211	2.47105	0.0449
	291.35	−9.35162	4.43935	−0.74553	2.31469	0.0452
ΔR_m	283.15	−0.16676	0.01314	−0.00209	0.07228	0.0019
	286.15	−0.16407	0.01404	−0.00360	0.05533	0.0022
	288.15	−0.15730	0.01879	0.00314	0.05108	0.0018
	290.15	−0.14490	0.02537	0.00616	0.03617	0.0017
	291.15	−0.13676	0.03641	0.00668	0.01978	0.0021
	291.35	−0.13651	0.03503	0.01248	0.02634	0.0021

chemical effects contribute negative values of V^E. The structural effects that arise from the geometrical fitting of one component into the other are due to the different molar volumes and free volumes of pure components and negative contributions to V^E. This negative excess molar volume V^E is an indication of strong heteromolecular interaction in the liquid mixtures and is attributed to change-transfer, dipole–dipole interactions and hydrogen bonding between the unlike molecules. The magnitudes of the contribution will vary with the components and composition of the mixtures. In the present investigation, the *TEA–W* mixture gave a negative magnitude of V^E, and they depict the presence of heteromolecular interaction.

(b) Refractive index mixing rules

The experimental refractive indices of the binary mixtures were also compared with the values calculated using the mixing rules proposed by Arago–Biot (AB) [14], Gladstone–Dale (GD) [11], Laplace (LP) [12], Lorentz–Lorenz [9,10], Eykman (EK) [13] and Oster (OST) [15].

$$\mathrm{AB}: n = \sum_{i=1}^{N} (\phi_i n_i), \tag{5}$$

$$\mathrm{GD}: n - 1 = \sum_{i=1}^{N} \{\phi_i (n_i - 1)\}, \tag{6}$$

$$\mathrm{LP}: n^2 - 1 = \sum_{i=1}^{N} \{\phi_i (n_i^2 - 1)\}, \tag{7}$$

Table 3. RMSD for the AB, GD, LP, LL, EK and OST equations.

	Temperature					
Equation	283.15 K	286.15 K	288.15 K	290.15 K	291.15 K	291.35 K
AB	5.98×10^{-3}	6.18×10^{-3}	6.31×10^{-3}	6.53×10^{-3}	6.57×10^{-3}	6.62×10^{-3}
GD	5.99×10^{-3}	6.18×10^{-3}	6.31×10^{-3}	6.54×10^{-3}	6.57×10^{-3}	6.62×10^{-3}
LP	1.57×10^{-2}	1.63×10^{-2}	1.69×10^{-2}	1.74×10^{-2}	1.77×10^{-2}	1.77×10^{-2}
LL	3.43×10^{-3}	3.53×10^{-3}	3.59×10^{-3}	3.71×10^{-3}	3.73×10^{-3}	3.76×10^{-3}
EK	7.52×10^{-3}	7.81×10^{-3}	8.04×10^{-3}	8.29×10^{-3}	8.41×10^{-3}	8.41×10^{-3}
OST	9.83×10^{-3}	1.01×10^{-2}	1.03×10^{-2}	1.06×10^{-2}	1.08×10^{-2}	1.08×10^{-2}

$$\mathrm{LL}: \frac{n^2-1}{n^2+2} = \sum_{i=1}^{N} \left\{ \phi_i \left(\frac{n_i^2-1}{n_i^2+2} \right) \right\}, \tag{8}$$

$$\mathrm{EK}: \frac{n^2-1}{n+0.4} = \sum_{i=1}^{N} \left\{ \phi_i \left(\frac{n_i^2-1}{n_i+0.4} \right) \right\}, \tag{9}$$

$$\mathrm{OST}: \frac{(n^2-1)-(2n^2+1)}{n^2} = \sum_{i=1}^{N} \left\{ \phi_i \left(\frac{(n_i^2-1)-(2n_i^2+1)}{n_i^2} \right) \right\}. \tag{10}$$

Experimental refractive indices were compared with those predicted by these mixing rules. The root mean square deviations (RMSD) between experimental and predicted n values are defined as:

$$\mathrm{RMSD} = \left(\frac{1}{N} \sum_i (n_{i,\mathrm{exptl}} - n_{i,\mathrm{pred}})^2 \right)^{1/2}, \tag{11}$$

where N is the number of experimental data.

In Table 3, the RMSD of the calculated values are presented. As RMSD values indicate, refractive indices are predicted with good accuracy for the mixture studied in this work. We can notice that the Lorentz–Lorenz relationship is the most suitable for the calculated refractive indices, and the highest deviations are obtained using the Laplace equation.

(c) Molar refraction and excess molar refraction

With the aim of gathering further information about the specific intermolecular interactions in the studied binary mixture, we have investigated the molar refraction R_m, defined by the Lorentz–Lorenz equation [22]:

$$R_m = \frac{n^2-1}{n^2+2} V_m, \tag{12}$$

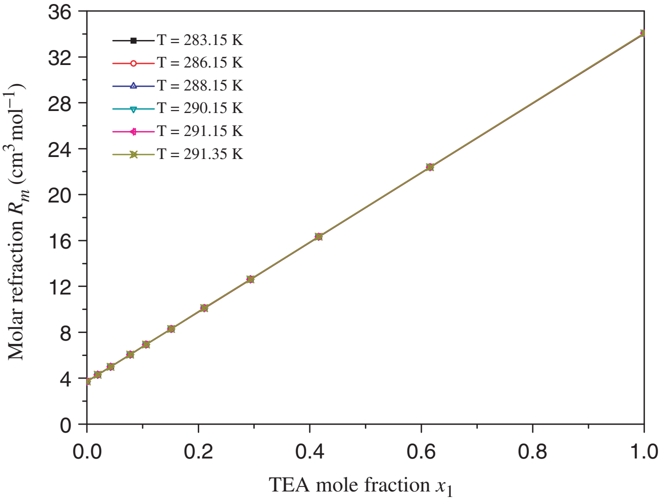

Figure 3. Molar refraction R_m, for *TEA-W* water mixture at 283.15, 286.15, 288.15, 290.15, 291.15 and 291.35 K as a function of TEA mole fraction x_1 (colour online).

where V_m is the molar volume of liquid. It must be remembered that R_m is a computed property strictly related to the electronic mean molecular polarisability, α, of a real system (either pure species or mixed components) by the equation:

$$R_m = \frac{\mathrm{N_A}\alpha}{3\varepsilon_0}, \tag{13}$$

where $\mathrm{N_A}$ is the Avogadro constant, ε_0 is the permittivity of free space and α is the mean polarisability of the liquid.

Generally, the polarisability α consists of two contributions, the first one measuring the ability with which the molecules will be deformed by an electric field, and the other due to the orientation of the molecular dipoles under the action of this field. The second effect depends on the temperature, whereas the first is practically temperature independent. The higher the permanent electric dipole moment of molecules, the more important are the orientational effects. Since we measured the refractive index in the optical region, the polarisability should not include orientational effects. Therefore, the molar refraction should not depend on temperature over a small temperature range, as can be seen in Figure 3. This shows that R_m values can, in fact, be associated with electronic polarisabilities. The R_m values obtained for the *TEA–W* solution lie in the range 3.710 cm^3 mol^{-1} (pure water at 283.15 K) to 34.050 cm^3 mol^{-1} (pure TEA at 291.35 K). Figure 3 reproduces the experimental trend of R_m *versus* x_1 for the investigated system from 283.15 to 291.35 K. This plot shows that the R_m profiles and, as a consequence, the electronic polarisation of the mixture, increase monotonously only with TEA mole fraction. As can be seen in Table 4, the polarisability of the *TEA–W* mixture is not affected by the temperature variation in the range selected.

Starting from the R_m data, it is possible to study the related excess quantity ΔR. There is no general rule for calculating this excess molar refraction function. Many authors [23–25]

Table 4. Molar refractions, R_m ($cm^3 mol^{-1}$), and the polarizability, $\alpha \times 10^{23}$ ($cm^3 mol^{-1}$), for the mixture *TEA-W* at 283.15, 286.15, 288.15, 290.15, 291.15 and 291.35 K.

	283.15 K		286.15 K		288.15 K		290.15 K		291.15 K		291.35 K	
x_1	R_m	α	R_m	α	R_m	α	R_m	α	R_m	α	R_m	α
0.000	3.710	0.1471	3.710	0.1471	3.709	0.1470	3.709	0.1470	3.709	0.1470	3.709	0.1470
0.019	4.298	0.1704	4.297	0.1703	4.297	0.1703	4.297	0.1703	4.297	0.1703	4.297	0.1703
0.042	5.001	0.1982	5.000	0.1982	5.001	0.1982	5.001	0.1982	5.001	0.1982	5.001	0.1982
0.077	6.061	0.2403	6.061	0.2403	6.062	0.2403	6.062	0.2403	6.063	0.2403	6.063	0.2403
0.106	6.923	0.2744	6.924	0.2745	6.925	0.2745	6.925	0.2745	6.926	0.2746	6.926	0.2746
0.151	8.287	0.3285	8.288	0.3286	8.290	0.3286	8.290	0.3286	8.291	0.3287	8.291	0.3287
0.211	10.094	0.4001	10.095	0.4002	10.097	0.4003	10.098	0.4003	10.100	0.4004	10.100	0.4004
0.293	12.600	0.4995	12.602	0.4996	12.605	0.4997	12.607	0.4998	12.609	0.4998	12.609	0.4998
0.416	16.310	0.6466	16.312	0.6466	16.318	0.6469	16.320	0.6470	16.323	0.6471	16.323	0.6471
0.615	22.365	0.8866	22.369	0.8868	22.378	0.8871	22.380	0.8872	22.385	0.8874	22.385	0.8874
1.000	34.018	1.3486	34.025	1.3488	34.038	1.3493	34.043	1.3495	34.050	1.3498	34.050	1.3498

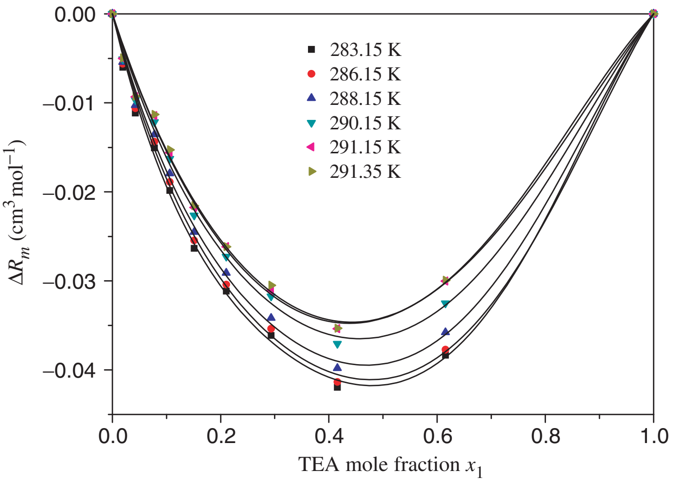

Figure 4. Excess molar refraction, ΔR_m, for *TEA-W* water mixture at 283.15, 286.15, 288.15, 290.15, 291.15 and 291.35 K as a function of TEA mole fraction x_1 (colour online).
Note: The solid lines represent the values calculated from the smoothing Equation 3.

make use of volume fractions ϕ instead of mole fractions x. ΔR_x and ΔR_ϕ differ largely from each other, so much so that they can even have different signs [23–27]. The departure from additivity of a volume property must be calculated by a method that expresses concentrations in which the property is expected to be additive [18,28]. The molar volume of an ideal system is additive when composition is expressed in mole fractions. If the molar refraction, which is isomorphic to a molar volume, is visualised as the hard-core volume of a mole of liquid, its conservation during the mixing of components should also be stated on the basis of the mole fraction scale.

The R_m data of the mixture have been used to calculate excess molar refraction, ΔR_m, using

$$\Delta R_m = R_m - \left(x_1 R_m^1 + x_2 R_m^2\right), \tag{14}$$

where R_m^1 and R_m^2 are molar refractions of the mixed pure components. The molar refraction of a pure component i is calculated using:

$$R_m^i = \frac{n_i^2 - 1}{n_i^2 + 2} V_i. \tag{15}$$

The results of the analysis of ΔR_m are plotted in Figure 4, where the curves at each temperature have also been represented by the Redlich–Kister equation, whose empirical coefficients A_i are listed in Table 2. The excess molar refraction ΔR_m, as calculated from Equation (14), represents the electronic perturbation due to orbital mixing of the molecules, and has been discussed extensively in the literature [29–35]. Figure 4 shows that ΔR_m values are negative for the *TEA–W* mixture at all temperatures tested. The values of V^E and ΔR_m support each other. The V^E and ΔR_m values become more negative at lower temperatures for both the mixtures, suggesting an increase in interaction between unlike molecules. In the $TEA-W$ mixture, there are many suggestions about the possible associations of TEA and water molecules. Among these suggestions, each TEA molecule is associated to two water molecules, the first forming an ammonium hydroxide derivative and the second being hydrogen bonded [36–38]. According to the work of Zhanpeisov *et al.* [39], in the (water)$_4$–TEA system, the water molecules form self-associated water chains centred in the *N*-site, with the tail-end water molecules forming very weak interactions with the methyl and methylene groups. Recently, by the Fourier Transformed InfraRed (FTIR) spectra of *TEA–W* mixtures in the OH stretching region, Muñoz *et al.* [40] suggested the formation of clusters containing tens of three- and four-coordinated water molecules; these molecules interact as an acceptor–acceptor through their oxygen atoms with two adjacent water molecules of the cluster, and as an H-donor with the electron pair of the nitrogen atom of TEA.

A final remark concerns the vicinity of critical temperature. One can clearly see from close observation of Figures 1–4 that V^E, Δn, R_m and ΔR_m have not been affected by the correlation of the concentration fluctuations. Indeed, we did not detect any anomaly near the critical composition $x_c = 0.0776$ mole fraction of TEA. Consequently, there will be a significant degree of hydrogen bonding, leading to strong correlation between molecules.

4. Conclusion

In this article, the densities and refractive index of *TEA–W* mixture are reported at 283.15, 286.15, 288.15, 290.15, 291.15 and 291.35 K as a function of TEA composition under atmospheric pressure. From these data, excess molar volumes, V^E, deviations in refractive index, Δn, and excess molar refraction, ΔR_m, have been computed, and were correlated by the Redlich–Kister-type equation. In all cases, for each TEA composition, both the absolute excess molar volumes and excess molar refraction noticeably increase over the entire mole fraction with a decrease of temperature from 291.35 to 283.15 K. These results are discussed in terms of molecular interactions between the mixing components. Furthermore, we have obtained no dependence of the corresponding molar refraction calculated using the Lorentz–Lorenz relation on temperature. Such data should be useful in industrial and chemical areas.

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