Full Length Research Paper

Molecular Radius, Molar Refraction, Polarizability and Internal Pressure Studies on THP + 1-Hexanol at Different Temperatures – Molecular Interactions

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Abstract. Molar refraction (R_m), molecular radii (r), polarizability (α) and internal pressure (π_i) values determined from the refractive index data for the binary liquid mixture of Tetrahydropyran (THP) with 1-hexanol have been measured at five temperatures (T=298.15, 303.15, 308.15, 313.15 and 318.15 K). The measured data utilized to evaluate the excess molar refraction (R_m^E), excess molecular radii (r^E), excess polarizability (α^E) and excess internal pressure (π_i^E) along with their Redlich–Kister co-efficient and standard error values of the mixed solvents. The results show existence of weak molecular interaction in the mixture.

Keywords: Molar refraction, molecular radii, internal pressure, excess parameters, THP, 1-hexanol

1. INTRODUCTION

Molecular radii (r), molar refraction (R_m) are important parameters of pure liquids and liquid mixtures. Both these parameters can be reduced with the help of refractive index and molar volume of a liquid mixture. They reflects structural features of the mixture; molecular radii tells about whether the neighboring molecules nearer or far away in the mixture. Molar refraction of a mixture will tell about actual volume of the mixture per mole i.e. the resultant mixture is of compact volume leading to association of molecules or bigger volume telling about disassociation of molecules in the mixture. The refractive index 'n' is a dimensionless optical property and is very sensitive to changes in the molecular association of pure liquids, solutions and mixtures. The factors 'R_m & n' are important in telling about polarizability (α) of a molecule in a mixture. Liquids in their mixtures behave differently than they behave individually. Many researchers like (Mahajan, 1997; Sonar et al., 2010; Rupali Talegaonkar, 2011; Ubarhande, 2011; Meenachi, 2012) have studied the molar refraction and polarizability constant of substituted heterocyclic compounds in different media from refractive indices. Both r, n of liquid/ liquid mixtures are of important work in engineering and science. These values depend on the temperature variations.

Also, several attempts have been made by different authors with empirical formulae to predict theoretical values of molecular radii (r) and refractive index (n) of liquid and liquid mixtures. In the present study author has made an attempt for the above said parameters on the binary mixture THP + 1-hexanol with entire mole fraction range of THP at five different temperatures (T=298.15, 303.15, 308.15, 313.15 and 318.15 K) using Anton Paar DSA 5000 and Abbemat refractometer. In continuation of the work, authors reported (Anil Kumar et al., 2014) excess molar volumes of the mixture for the same binary system at five different temperatures as given above in their paper "Excess parameter studies on tetrahydropyran with 1-hexanol at T = 298.15 to 318.15 K using Anton Paar"

Knowing refractive index, molar volume, molecular radii with the help of empirical formulae relation we can estimate internal pressure (π_i) of a mixture also.

2. EXPERIMENTAL DETAILS

Measurements of THP and 1-hexanol with mass fraction purities >0.998 were purchased from Sigma Aldrich chemical company, the chemicals were kept in airtight glass bottles were performed in an isothermal mode; i.e. the measurements of all prepared solution were done at the same particular

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temperature, then the temperature was changed and the measurements were repeated. The refractive indices were determined using an Abbemat refractometer - HP Dr. Kernchen supplied by Anton Paar that also has a temperature controller that keeps the samples at working temperature. The uncertainties in the temperature and refractive index values are ± 0.01 K and $\pm 1 \times 10^{-5}$, respectively. The binary mixture mole fractions are prepared by weighing; using a Sartorius balance with an uncertainty of $\pm 1 \times 10^{-2}$ mg and the uncertainties in the mole fraction of the prepared mixtures were estimated to be $\pm 1 \times 10^{-4}$.

Table 1: Molar refraction (R_m), Molecular radius (r), Polarizability (α), Internal pressure (π_i) with there Excess values along with Coefficients (A_0, A_1, A_2, A_3, and A_4) of the Redlich-Kister equation and standard deviation (σ) at various mole fractions of THP + 1-hexanol mixtures at 298.15 K

x_1	$10^{-3} R_m$ $m^3 mol^{-1}$	$10^{-9} r$ m	α $m^3 mol^{-1}$	$10^4 \pi_i$ pa
		298.15 K		
0.0000	26.4814	4.7230	1.0535	0.7755
0.1335	26.9537	4.7509	1.0723	0.7627
0.2445	27.3084	4.7716	1.0864	0.7531
0.3547	27.6483	4.7913	1.0999	0.7442
0.4506	27.9486	4.8086	1.1119	0.7366
0.5620	28.2438	4.8255	1.1236	0.7295
0.6602	28.5072	4.8405	1.1341	0.7233
0.7436	28.6713	4.8497	1.1406	0.7191
0.8447	28.9617	4.8660	1.1522	0.7135
0.9073	29.1018	4.8739	1.1578	0.7108
1.0000	29.3095	4.8854	1.1660	0.7074
		298.15 K		
x_1	$10^{-3} R_m^E$ $m^3 mol^{-1}$	$10^{-9} r^E$ m	α^E $m^3 mol^{-1}$	$10^4 \pi_i^E$ pa
0.0000	0.0000	0.0000	0.0000	0.0000
0.1335	0.0966	0.0063	0.0039	-0.0037
0.2445	0.1310	0.0086	0.0052	-0.0057
0.3547	0.1692	0.0110	0.0067	-0.0073
0.4506	0.1894	0.0123	0.0075	-0.0080
0.5620	0.1788	0.0116	0.0071	-0.0079
0.6602	0.1424	0.0093	0.0057	-0.0070
0.7436	0.1070	0.0070	0.0043	-0.0059
0.8447	0.0765	0.0050	0.0030	-0.0043
0.9073	0.0614	0.0039	0.0025	-0.0030
1.0000	0.0000	0.0000	0.0000	0.0000
		298.15 K		
A_0	0.7585	0.0490	0.0302	-0.0323
A_1	0.1540	0.0102	0.0060	-0.0010
A_2	-0.8854	-0.0518	-0.0358	0.0101
A_3	-0.0121	-0.0006	0.0000	0.0037
A_4	1.5387	0.0900	0.0625	-0.0208
$10^2 (\sigma)$	1.3164	0.0746	0.0501	0.0203

Table 2: Molar refraction (R_m), Molecular radius (r), Polarizability (α), Internal pressure (π_i) with there Excess values along with Coefficients (A_0, A_1, A_2, A_3, and A_4) of the Redlich-Kister equation and standard deviation (σ) at various mole fractions of THP + 1-hexanol mixtures at 303.15 K

x_1	$10^{-3} R_m$ $m^3 mol^{-1}$	$10^{-9} r$ m	α $m^3 mol^{-1}$	$10^4 \pi_i$ pa
		303.15 K		
0.0000	26.4953	4.7238	1.0541	0.7827
0.1335	26.9614	4.7513	1.0726	0.7694
0.2445	27.3177	4.7722	1.0868	0.7596
0.3547	27.6583	4.7919	1.1003	0.7505
0.4506	27.9574	4.8091	1.1122	0.7426
0.5620	28.2498	4.8258	1.1239	0.7353
0.6602	28.5138	4.8408	1.1344	0.7288
0.7436	28.6778	4.8501	1.1409	0.7245
0.8447	28.9695	4.8665	1.1525	0.7186
0.9073	29.1093	4.8743	1.1581	0.7158
1.0000	29.3237	4.8862	1.1666	0.7122
		303.15 K		

x_1	$10^{-3} R_m^E$ m^{3}mol^{-1}	$10^{-9} r^E$ m	α^E m^{3}mol^{-1}	$10^4 \pi_i^E$ pa
0.0000	0.0000	0.0000	0.0000	0.0000
0.1335	0.0900	0.0060	0.0036	-0.0038
0.2445	0.1269	0.0085	0.0051	-0.0058
0.3547	0.1651	0.0108	0.0066	-0.0073
0.4506	0.1836	0.0119	0.0073	-0.0081
0.5620	0.1713	0.0111	0.0068	-0.0080
0.6602	0.1347	0.0089	0.0054	-0.0071
0.7436	0.0996	0.0067	0.0040	-0.0060
0.8447	0.0694	0.0046	0.0028	-0.0044
0.9073	0.0551	0.0035	0.0022	-0.0031
1.0000	0.0000	0.0000	0.0000	0.0000
		303.15 K		
A_0	0.7318	0.0474	0.0292	-0.0327
A_1	0.1856	0.0117	0.0075	-0.0006
A_2	-0.8628	-0.0481	-0.0344	0.0116
A_3	-0.0673	-0.0026	-0.0035	0.0032
A_4	1.3874	0.0787	0.0546	-0.0248
$10^2 (\sigma)$	1.3452	0.0765	0.0520	0.0198

Table 3: Molar refraction (R_m), Molecular radius (r), Polarizability (α), Internal pressure (π_i) with there Excess values along with Coefficients (A_0, A_1, A_2, A_3, and A_4) of the Redlich-Kister equation and standard deviation (σ) at various mole fractions of THP + 1-hexanol mixtures at 308.15 K

x_1	$10^{-3} R_m$ m^{3}mol^{-1}	$10^{-9} r$ m	α m^{3}mol^{-1}	$10^4 \pi_i$ pa
		308.15 K		
0.0000	26.5057	4.7244	1.0545	0.7895
0.1335	26.9610	4.7513	1.0726	0.7758
0.2445	27.3178	4.7722	1.0868	0.7658
0.3547	27.6585	4.7919	1.1004	0.7564
0.4506	27.9611	4.8093	1.1124	0.7484
0.5620	28.2524	4.8260	1.1240	0.7407
0.6602	28.5171	4.8410	1.1345	0.7341
0.7436	28.6849	4.8505	1.1412	0.7296
0.8447	28.9723	4.8666	1.1526	0.7234
0.9073	29.1162	4.8747	1.1583	0.7205
1.0000	29.3341	4.8868	1.1670	0.7168
		308.15 K		

x_1	$10^{-3} R_m^E$ m^{3}mol^{-1}	$10^{-9} r^E$ m	α^E m^{3}mol^{-1}	$10^4 \pi_i^E$ pa
0.0000	0.0000	0.0000	0.0000	0.0000
0.1335	0.0793	0.0053	0.0032	-0.0040
0.2445	0.1162	0.0078	0.0046	-0.0060
0.3547	0.1557	0.0103	0.0062	-0.0075
0.4506	0.1755	0.0115	0.0070	-0.0082
0.5620	0.1644	0.0107	0.0065	-0.0081
0.6602	0.1287	0.0085	0.0051	-0.0072
0.7436	0.0941	0.0063	0.0037	-0.0061
0.8447	0.0642	0.0043	0.0026	-0.0044
0.9073	0.0506	0.0032	0.0020	-0.0032
1.0000	0.0000	0.0000	0.0000	0.0000
		308.15 K		
A_0	0.7014	0.0457	0.0278	-0.0331
A_1	0.1635	0.0109	0.0067	-0.0008
A_2	-0.8965	-0.0506	-0.0358	0.0109
A_3	-0.0880	-0.0051	-0.0040	0.0018
A_4	1.3179	0.0738	0.0536	-0.0259
$10^2 (\sigma)$	1.2377	0.0709	0.0502	0.0228

3. THEORY

Pandey et al. (2004) used several empirical relations based on acoustic methods to calculate the molecular radii of liquid mixtures. Molecular radii (r) of the pure liquids or binary mixtures are;

$$r = \left[\frac{3}{4\pi N} V_m \frac{n^2 - 1}{n^2 + 2} \right]^{1/3} \quad (1)$$

From the measured values of refractive indices molar refraction (R_m) is calculated using the relation,

$$R_m = \left[\frac{n^2-1}{n^2+2}\right]V_m \tag{2}$$

Polarizability (α) by the Lorentz-Lorentz relation given as:

$$\left(\frac{n^2-1}{n^2+2}\right) = \left(\frac{4}{3}\right)\pi n^1 \alpha \tag{3}$$

Where $n^1 = (N/V_m)$, N is Avogadro's constant and V_m is the molar volume.

Also, (Hirschfelder et al., 1964) Curties equation of state, the internal pressure of a mixture is

$$\pi_{int} = \frac{2^{\frac{1}{6}}RT}{2^{\frac{1}{6}}V_m - 2rN^{\frac{1}{3}}V_m^{2/3}} \tag{4}$$

Where V_m- Molar volume, R_m- molar refraction and r- molecular radii.

The strength of interaction between the component molecules of binary liquid system is well reflected in the excess functions from ideality. The excess thermodynamic properties such as R_m^E, r^E, α^E and π_i^E have been calculated using the following equation

$$Y^E = Y_{mix} - (x_1 y_1 + x_2 y_2) \tag{5}$$

where x_1 and x_2 are mole fractions of THP and 1-hexanol respectively.

The excess parameters were fitted to Redlich – Kister polynomial (Redlich O, 1948) equation to estimate the adjustable parameters.

$$Y^E = x_1 x_2 \sum_{i=0}^{n} a_i (1-2x)^i \tag{6}$$

Using least-squares regression method, the (a_i) coefficients are obtained by fitting above equation to the experimental values. The optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ)

$$\sigma(Y) = \left[\frac{\sum(Y_{expt} - Y_{calc})^2}{N-n}\right]^{1/2} \tag{7}$$

where 'N' is the number of data points and 'n' is the degree of fitting, (i.e. number of coefficients).

4. RESULTS AND DISCUSSIONS

Tables 1 to 5, encloses the derived parameters viz., molar refraction (R_m), molecular radii (r), polarizability (α) and internal pressure (π_i) along with their excess parameters, Redlich–Kister co-efficient and standard error values at five different temperatures studied over entire mole fraction range of THP. In the earlier paper (Anil Kumar K 2014) the author has studied the same binary mixture (THP+1-hexanol binary mixture) it was reported that excess values of V_m^E positive and Z^E as negative which tells about the presence of weak dipole-dipole interactions between the component molecules of the mixture.

Now, in the present work, on close perusal of the tables, reveals there is an increasing trend of R_m, r and α values for the binary mixture with respect to increase of mole fraction of THP. Increase of 'r' tells that size of the molecule in the mixture increases and hence actual volume of the mixture per mole R_m also increases. As size of the molecule increases it results in the displacement of electron in the molecules of the mixture and hence more polarizability. This leads to dipole-dipole interactions. But, the smaller magnitude of r and α values show weak dipole-dipole interactions in the present work. Further, the internal pressure calculated from empirical formula shows a decreasing trend of values with respect to increase of mole fraction of THP, which results decrease of attraction between hetero molecules in the mixture. Also, the excess functions give an idea about the extent to which the given liquid mixtures deviate from ideality. These excess properties are fundamentally important in understanding the intermolecular interactions and nature of molecular campaigning in hetero molecules. The above tables, shows the R_m^E, r^E, α^E and π_i^E values of the binary mixture with Redlich–Kister polynomial coefficients.

Table 4: Molar refraction (R_m), Molecular radius (r), Polarizability (α), Internal pressure (π_i) with there Excess values along with Coefficients (A_0, A_1, A_2, A_3, and A_4) of the Redlich-Kister equation and standard deviation (σ) at various mole fractions of THP + 1-hexanol mixtures at 313.15 K

x_1	$10^{-3} R_m$ m³mol⁻¹	10^{-9} r m	α m³mol⁻¹	$10^4 \pi_i$ pa
		313.15 K		
0.0000	26.5131	4.7248	1.0548	0.7961
0.1335	26.9657	4.7516	1.0728	0.7820
0.2445	27.3253	4.7726	1.0871	0.7718
0.3547	27.6653	4.7923	1.1006	0.7622
0.4506	27.9679	4.8097	1.1127	0.7539
0.5620	28.2565	4.8262	1.1241	0.7460
0.6602	28.5195	4.8411	1.1346	0.7391

x₁			
0.7436	28.6958	4.8511	1.1416	0.7346
0.8447	28.9799	4.8671	1.1529	0.7281
0.9073	29.1219	4.8750	1.1586	0.7250
1.0000	29.3421	4.8873	1.1673	0.7211

313.15 K

x_1	$10^{-3} R_m^E$ $m^3 mol^{-1}$	$10^{-9} r^E$ m	α^E $m^3 mol^{-1}$	$10^4 \pi_i^E$ pa
0.0000	0.0000	0.0000	0.0000	0.0000
0.1335	0.0761	0.0052	0.0030	-0.0040
0.2445	0.1170	0.0079	0.0046	-0.0059
0.3547	0.1556	0.0103	0.0062	-0.0074
0.4506	0.1728	0.0113	0.0069	-0.0082
0.5620	0.1607	0.0105	0.0064	-0.0081
0.6602	0.1269	0.0084	0.0050	-0.0072
0.7436	0.0940	0.0063	0.0037	-0.0060
0.8447	0.0640	0.0043	0.0026	-0.0044
0.9073	0.0491	0.0032	0.0020	-0.0031
1.0000	0.0000	0.0000	0.0000	0.0000

313.15 K

A_0	0.6872	0.0448	0.0274	-0.0333
A_1	0.1851	0.0120	0.0076	-0.0003
A_2	-0.7691	-0.0426	-0.0318	0.0144
A_3	-0.1568	-0.0087	-0.0068	0.0001
A_4	1.0730	0.0598	0.0454	-0.0308
$10^2 (\sigma)$	1.1188	0.0627	0.0462	0.0246

Table 5: Molar refraction (R_m), Molecular radius (r), Polarizability (α), Internal pressure (π_i) with there Excess values along with Coefficients (A_0, A_1, A_2, A_3, and A_4) of the Redlich-Kister equation and standard deviation (σ) at various mole fractions of THP + 1-hexanol mixtures at 318.15 K

x_1	$10^{-3} R_m$ $m^3 mol^{-1}$	$10^{-9} r$ m	α $m^3 mol^{-1}$	$10^4 \pi_i$ pa
		318.15 K		
0.0000	26.5226	4.7254	1.0552	0.8025
0.1335	26.9710	4.7519	1.0730	0.7881
0.2445	27.3290	4.7728	1.0872	0.7776
0.3547	27.6726	4.7928	1.1009	0.7678
0.4506	27.9743	4.8101	1.1129	0.7592
0.5620	28.2660	4.8268	1.1245	0.7512
0.6602	28.5270	4.8416	1.1349	0.7440
0.7436	28.7054	4.8516	1.1420	0.7393
0.8447	28.9875	4.8675	1.1532	0.7325
0.9073	29.1313	4.8755	1.1589	0.7294
1.0000	29.3549	4.8880	1.1678	0.7253

318.15 K

x_1	$10^{-3} R_m^E$ $m^3 mol^{-1}$	$10^{-9} r^E$ m	α^E $m^3 mol^{-1}$	$10^4 \pi_i^E$ pa
0.0000	0.0000	0.0000	0.0000	0.0000
0.1335	0.0709	0.0048	0.0028	-0.0041
0.2445	0.1112	0.0076	0.0044	-0.0059
0.3547	0.1509	0.0100	0.0060	-0.0074
0.4506	0.1693	0.0111	0.0067	-0.0082
0.5620	0.1579	0.0103	0.0063	-0.0081
0.6602	0.1238	0.0082	0.0050	-0.0072
0.7436	0.0903	0.0061	0.0036	-0.0060
0.8447	0.0600	0.0041	0.0024	-0.0044
0.9073	0.0457	0.0030	0.0018	-0.0032
1.0000	0.0000	0.0000	0.0000	0.0000

318.15 K

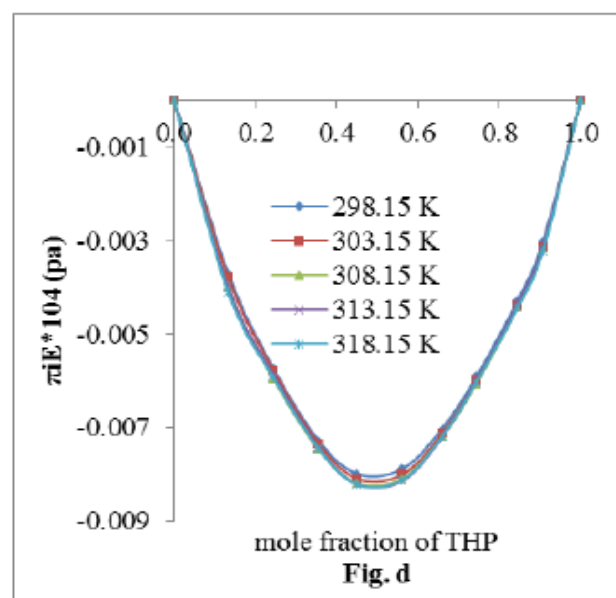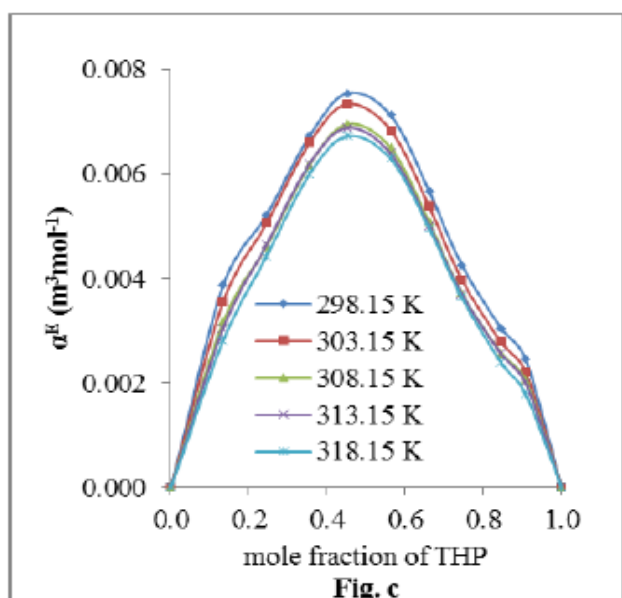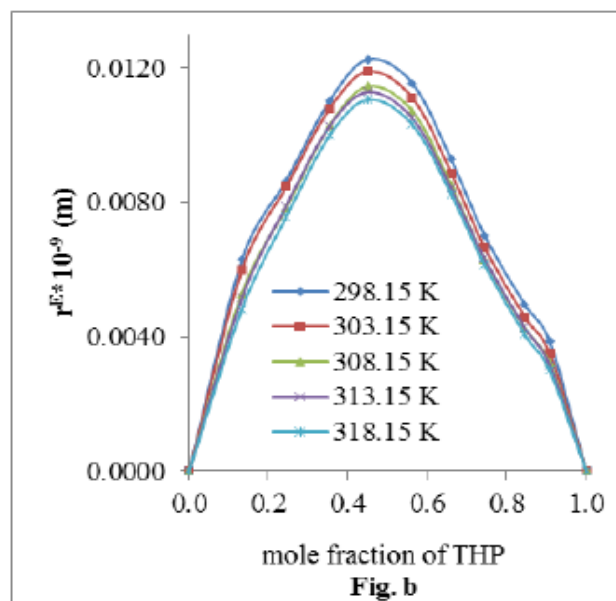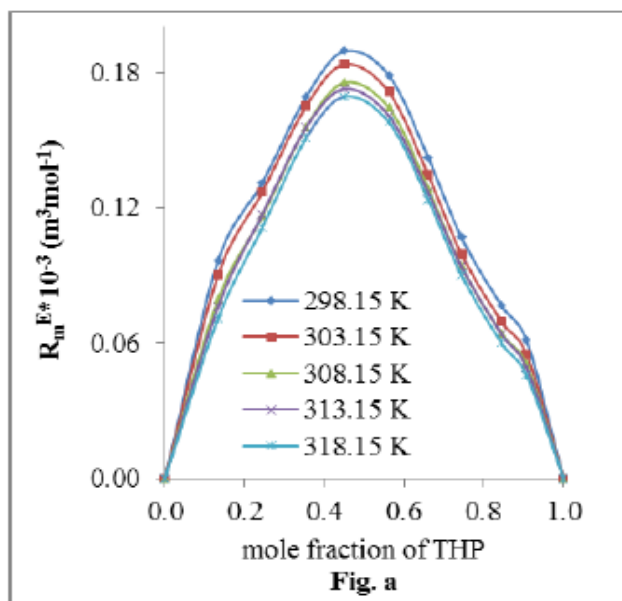|				
A_0	0.6750	0.0440	0.0268	-0.0333
A_1	0.1716	0.0112	0.0065	-0.0006
A_2	-0.8238	-0.0445	-0.0315	0.0137
A_3	-0.1452	-0.0086	-0.0051	0.0005
A_4	1.0823	0.0584	0.0404	-0.0328
$10^2 (\sigma)$	1.0157	0.0561	0.0414	0.0256

Fig. 1: a-d: Molar refraction (R_m^E), molecular radius (r^E), polarizability (α^E) and internal pressure (π_i^E) with the mole fraction of THP + 1-hexanol at different temperatures

Figures 1 revels R_m^E, r^E and α^E are positive, while π_i^E values shows reverse trend over the whole composition range. R_m^E represents the electronic perturbation due to orbital mixing of two components and gives information regarding the strength of interaction in mixture. The positive deviation of R_m^E and α^E suggests the dipole–dipole and donor–acceptor interaction between unlike molecules of the mixture. The negative deviations in π_i^E indicate the decreasing nature of attractive interactions in the mixture. It is well supported by positive values of excess inter molecular radii (r^E). These results indicate the presence of weak intermolecular interactions in the mixture.

5. CONCLUSION

Knowing molar volume, refractive index for a binary mixture at different temperatures, we can measure molar refraction, molecular radii, polarizability and internal pressure. The positive deviations of R_m^E, α^E, r^E and negative deviations of π_i^E indicate the presence of weak intermolecular interactions in the mixture.

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