ISROSET- International Journal of Scientific Research in Chemical Sciences
Research Paper Volume-3, Issue-1 ISSN: 2455-3174

Refractive Properties of Binary Mixtures of 1,4-Butanediol with Methylpyridine Isomers

J. V .Srinivasu[a,*], K. Narendra[b], and B.SubbaRao[c]

[a] *Sri Vishnu Engineering College for Women,Bhimavaram-534 202, India.srinivas.jaddu@gmail.com*
[b] *V R Siddhartha Engineering College,Vijayawada-520 007, India.narenk75@gmail.com*
[c] *VSR & NVR College,Tenali-522201, Andhra Pradesh, India.bezawadasubbarao1@gmail.com*

Available online at www.isroset.org

Received: Jan/12/2016 Revised: Jan/20/2016 Accepted: Feb/18/2016 Published: Feb29/2016

***Abstract*—**Refractive indices, n_D, and densities,ρ, have been measured for 1,4-butanediol (1,4-BD) + α-picoline/ β-picoline/ γ-picoline binary mixtures over the entire composition range at T = (303.15, 308.15, 313.15 and 318.15) K. Some empirical and theoretical relationships like, Arago-Biot (A-B), Eykman (E), Eyring and John (E-J), Gladstone-Dale (G-D), Heller (H), Lorentz-Lorenz (L-L), Newton (N), Oster (Os) and Weiner (W) have been applied to study the dependence of the measured and derived quantities on temperature and on binary composition. Furthermore, refractive index deviation, Δn_D, molar refraction, R, and molar refraction deviation, ΔR have been calculated. Results have been fitted to Redlich-Kister polynomial equation to obtain the adjustable parameters and standard deviations between the measured and fitted values, respectively. The results are discussed briefly.

Keywords-*1,4-butanediol, refractive index, picoline, binary system, refractive index mixing rules.*

I. INTRODUCTION

A small amount of sample is sufficient for the measurement of refractive index, n_D in wide ranges of temperatures with high precisions and gives information about intermolecular interactions; it is also closely related to other thermo physical properties [1-5]. Therefore, some solutions, whose properties are otherwise difficult to measure directly, can be more easily identified by knowing their n_D values.

As a part of a study on thermodynamic and physico-chemical properties of binary liquid mixtures containing 1,4-BD as one of the components [6], we report here some investigations about refractive properties (and some related parameters) of binary liquid mixtures of 1,4-BD with α-picoline, β-picoline and γ-picoline at different temperatures, T = (303.15, 308.15, 313.15 and 318.15) K. Results were fitted to obtain the adjustable parameters and standard deviations between the measured and fitted values, respectively. The Theoretical values of refractive index are evaluated by using Arago-Biot [7], Eykman [8], Eyring and John [9], Gladstone-Dale [10], Heller [11], Lorentz-Lorenz [12], Newton [13], Oster [14] and Weiner [15] relations and the average percentage deviation values have been given. The relative applicability of these mixing rules has been tested by many researchers [16-20]

1,4-BD is a clear viscous liquid, which is miscible with water and most polar organic solvents. The presence of two hydroxyl groups in vicinal positions (at the positions 1 and 4) of this diol makes it suitable as a useful chemical intermediate in the manufacture of many chemical products.

Picoline refers to three different methylpyridineisomers, all are colourless liquids at room temperature and pressure and are miscible with water and most organic solvents. α-picoline is used as an adhesive for textile tire cord and also a precursor to the agrochemical, nitrapyrin, which prevents loss of ammonia from fertilizers. β-picoline is a useful precursor to agrochemicals, such as chlorpyrifos and used to make antidotes for poisoning by organophosphate acetylcholinesterase inhibitors. γ-picoline is both isolated from coal tar and is synthesized industrially. It is formed via the reaction of acetaldehyde and ammonia in the presence of an oxide catalyst. It is also used in drugs.

Several related quantities have been calculated and presented graphically to enhance visual impact and to gain insight into the various interactions operating in the mixtures.

II. EXPERIMENTAL

1,4-BD and methylpyridine isomers (Sigma-Aldrich, USA, mass fraction purity 0.99) used in this study were purified by standard methods [21,22]. Before use, all

*Corresponding Author:
J. V. Srinivasu, srinivas.jaddu@gmail.com,
Shri Vishnu Engineering College for Women, India

© 2016, IJSRCS All Rights Reserved

chemicals were stored over 0.4nm molecular sieves for 72 hrs to remove the water content, if any, and were degassed at low pressure. Moreover, name of the chemical, source, CAS number, purification method and purity in mass fraction of the component liquids are given in Table-1.The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. All samples were prepared immediately prior to measurements using an electronic balance (CPA-225D, Sartorius, Germany) precisely within $\pm 1\times10^{-5}$g. The uncertainty in the mole fraction was estimated to be within $\pm 1\times10^{-4}$.

The densities of the pure liquids and their binary mixtures were measured by using a single-capillary pyconometer (made of Borosil glass) having a bulb capacity of ≈10mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The densities of pure water at the required temperature were taken from the literature [23]. The reproducibility of the density measurements was within ±2 x 10^{-5} g.cm^{-3}. The temperature of the test liquids during the measurements was maintained to an accuracy of ±0.02K in an electronically controlled thermostatic water bath (Julabo). The refractive index in pure liquids and in their binary mixtures were measured using an Abbe Refractometer. The refractive index data were reproducible within ±0.2.The reliability of experimental measurements of density and refractive index was ascertained by comparing the experimental data of the pure liquids with the corresponding literature values [24-26] at the studied temperatures. This comparison is given in Table-2 and the experimental and literature values compare well in general.

III. THEORY

Looking at the literature, it is possible to extract many equations and empirical or theoretical models, due to various authors, accounting for the dependence of refractive properties on binary composition of liquid mixtures. With the aim of checking the effectiveness of these equations when applied to the systems here investigated, we have made a speculative test in order to compare their relative merits, basing the judgement on the average difference between experimental values and those calculated by the selected relationships. The 'mixing rules' tested here are the following:

Arago-Biot (A-B), assuming volume addivity, proposed the following relaiton for refractive index of binary mixtures:

$$n_m = \phi_1 n_1 + \phi_2 n_2 \qquad (1)$$

Eykman's (E) relation is represented as:

$$\left(\frac{n_m^2-1}{n_m+0.4}\right)V_m = \left(\frac{n_1^2-1}{n_1-0.4}\right)\frac{M_1 x_1}{\rho_1} + \left(\frac{n_2^2-1}{n_2+0.4}\right)\frac{M_2 x_2}{\rho_2} \qquad (2)$$

where, symbols have their usual meaning.

Eyring and John (E-J) relation:

$$n = n_1\phi_1^2 + 2(n_1 n_2)^{1/2} + \phi_1\phi_2 + n_2\phi_2^2 \qquad (3)$$

Gladstone-dale (G-D) equation for predicting the refractive index of a binary mixture is as follows:

$$(n_m - 1) = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) \qquad (4)$$

Heller's (H) relation is given by:

$$\left(\frac{n_m - n_1}{n_1}\right) = \frac{3}{2}\left(\frac{m^2-1}{m^2+2}\right)\phi_2 \qquad (5)$$

where m = $\frac{n_2}{n_1}$

The Lorentz-Lorenz (L-L) relation for refractive index is based on the change in the molecular polarizability with volume fraction:

$$\left(\frac{n_m^2-1}{n_m^2+2}\right)\frac{1}{\rho_m} = \left(\frac{n_1^2-1}{n_1^2+2}\right)\frac{w_1}{\rho_1} + \left(\frac{n_2^2-1}{n_2^2+2}\right)\frac{w_2}{\rho_2} \qquad (6)$$

Newton (N) gave the following equation:

$$(n_m^2 - 1) = \phi_1(n_1^2 - 1) + \phi_2(n_2^2 - 1) \qquad (7)$$

Oster (Os) relation:

$$\frac{(n^2-1)(2n^2+1)}{n^2} = \frac{(n^2-1)(2n_1^2+1)}{n_1^2}\phi_1 + \frac{(n_2^2-1)(2n_2^2+1)}{n_2^2}\phi_2 \qquad (8)$$

Weiner's (W) relation is represented as:

$$\left(\frac{n_m^2 - n_1^2}{n_m + 2n_1^2}\right) = \left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\phi_2 \qquad (9)$$

In the above equations, n_m is the refractive index of the mixture; n_1 and n_2 are the refractive indices of the pure components 1 and 2 respectively. φ_i is volume fraction of component i. $\phi_i = x_i V_i / \sum x_i V_i$, V_i is the molar volume of component i and x_i is the mole fraction of component i.

With the aim of gathering further information about the specific intermolecular interactions in these binary systems, we have investigated the molar refraction, R, defined by the Lorentz-Lorenz equation:

$$R = \left(\frac{n_m^2 - 1}{n_m^2 + 2}\right)V_m \qquad (10)$$

where, $V_m = (x_1M_1 + x_2M_2)/\rho$ is the molar volume.

Δn_D and ΔR were calculated using the following equations:

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D_2} \qquad (11)$$

$$\Delta R = R - x_1 R_1 - x_2 R_2 \qquad (12)$$

where n_D is the refractive index of the mixture, x_i is the mole fraction, and R_i is the molar refraction of component i.

The deviations were further fitted to the Redlich-Kister polynomial equation [27]:

$$\Delta x = x_1(1 - x_1)\sum_{i=1}^{4} A_i(1 - 2x_1)^i \qquad (13)$$

© 2016, IJSRCS All Rights Reserved

where ΔX is the deviation in parameters and x_1 is the mole fraction of 1,4-BD. The values of Redlich-Kister polynomial coefficients, A_i, were evaluated by the method of least squares and the standard deviation σ (ΔX) was calculated as:

$$\sigma(\Delta x) = \left[\frac{\sum \left(X_{\exp t} - X_{cal} \right)^2}{n - m} \right]^{1/2} \quad (14)$$

where n and m are the number of data points and parameters, respectively.

The results obtained from Eq. (1)-(9) have been analyzed in terms of average percentage deviation (APD) calculated using the relation

$$APD = \frac{1}{m} \left[\sum \frac{\left(n_{D\,Expt} - n_{D\,Calc} \right)}{n_{D\,Expt}} \times 100 \right] \quad (15)$$

where *m* is number of data points

IV. RESULTS AND DISCUSSION

Experimental values of densities and refractive indices for the binary mixtures 1,4-BD + α-picoline, + β-picoline, + γ- picoline have been reported in Table-3 at temperatures T = (303.15-318.15) K over the entire mole fraction range. Variation of refractive index deviation, molar refraction, and molar refraction deviation with mole fraction of 1,4-BD have been shown in Figs. 1 (a to c) to 3 (a to c) respectively. The deviation parameters are fitted to Redlich-Kister equation, the adjustable parameters and standard deviations have been given in Table-4. Table-5 summarizes the APD values between the experimental n_D values and those calculated for each mixing rule. It is evident that all selected relations can be profitably used if only a rough approximation in predictive calculations is required.

From Table-5 it can be observed that the APD values are smaller for Eyring-John relation and larger for Oster relation, even if the relative merits of the checked equations are comparable in magnitude to each other. The equations used in this paper for investigation is limited to some literature models which can be applied when preliminary knowledge of liquid mixture density is available. Some other equations are also available for prediction of refractive indices but the applicability of those models needs the a priori knowledge of one or more empirical parameters other than density for each mixed liquid.

Figure-1 (a to c) shown the profiles of Δn_D against the mole fraction of 1,4-BD at each temperature. The trends are always positive for all the mixtures studied, with a sharp maximum centered at $x_1 = 0.5$ which becomes higher as temperature increases. The same trends have been observed at all temperatures studied. The maximum values may indicate the presence of a complex adduct. The Δn_D values are observed in the order 1,4-BD + β-picoline> 1,4-BD + α-picoline> 1,4-BD + γ-picoline at all temperatures studied.

The sign and magnitude of Δn_D also varies with the structural characteristics of the liquid components arising from the geometrical fitting of one component into the structure of other component due to the difference in the molecular size and shape of the components. If the unlike molecules have almost the same molar volumes, this effect should be significant. However, even if slight difference in

Table -1: Details of studied compounds, CAS number, source, purification method, purity and analysis method.

Chemical name	CAS number	Source	Purification method	Mass fraction purity	Analysis method
1,4 butanediol	110-63-4	Sigma Aldrich	Vacuum distillation	≥0.99	Gas chromatography
α-picoline	109-06-8	Sigma Aldrich	Vacuum distillation	≥0.99	Gas chromatography
β-picoline	108-99-6	Sigma Aldrich	Vacuum distillation	≥0.99	Gas chromatography
γ-picoline	108-89-4	Sigma Aldrich	Vacuum distillation	≥0.99	Gas chromatography

GC = Gas chromatography

The basis of these mixing rules of refractive index is Electromagnetic theory of light, which treats the molecules as dipoles or assemblies of dipoles by an external field. Refractive index dependent on the nature of liquid, pressure and temperature and is directly related to a number of physical parameters of the liquid such as dielectric constant, density, molar refractivity etc. Here an attempt has been made to study the validity of nine mixing rules for predicting the refractivity of binary liquid system, over the entire mole fraction range.

the free volume between different species could facilitate the penetration of one component into the other and as the difference of the free volumes of the two pure species increases, the more positive should be the contribution to Δn_D. The interstitial accommodation of the small molecules of 1,4-BD (V_m = 12.1 cm^3 mol^{-1} at 298.15 K) in the large methylpyridine isomers ($V_{m(\alpha\text{-pyridine})}$ = 79.2 cm^3 mol^{-1}, $V_{m(\beta\text{-}}$

© 2016, IJSRCS All Rights Reserved

$_{pyridine)}$ = 79.2 cm^3 mol^{-1} and $V_{m(\gamma\text{-pyridine})}$ = 97.4 cm^3 mol^{-1} at 298.15 K) will also make the deviations of Δn_D positive.

In general, the positive deviations in Δn_D values are considered due to the presence of significance interactions in the mixtures, whereas negative deviations in Δn_D values indicate weak interactions between the components of the mixture [28]. The observed trends (Figure-1 (a to c) and magnitudes of Δn_D values indicate the presence of significant interactions in all the mixtures taken up for the study. The deviation in Δn_D values are found opposite to the sign of excess molar volumes for all the three mixtures [6], which is in agreement with the view proposed by Brocos*et al*., [29].

With the aim of gathering further informations about the specific intermolecualr interactions in these binary mixtures, we have investigated the molar refraction R. It must be rembered that R is a computed property strictly related to the electronic polarizability (α) of a real system (either pure or mixed components) by the equation: $R = (4/3)\pi\alpha L$. Therefore any information related to quantity R can be parallely referred to the total electronic polarizability of the investigated system.

Thus R being affected by any variation of the chemical environment of a real species, its functional dependecne on temeprature and binary composition provides information about the intermolecualr interactions and driving forces acting on the liquid structure of the binary mixtures. The caluclated R values of pure components at T= 303.15 K are 2.3693 (1,4-BD), 2.9091 (α-picoline), 2.8926 (β-picoline), and 2.8948 (γ-picoline). Figure-2 (a to c) illustrates the R profile against x_1 for the three binary systems at four different temepratures. As it can be seen, the R values decreases with increase in concentration of 1,4-BD in all the sytems studied.

Table- 2: Comparison of densities, ρ, and refractive indices, n_D, of pure liquids with their literature values at T = 303.15, 308.15, 313.15 and 318.15K and atmospheric pressure 0.1Mpa.

Compound	T(K)	ρ/kg.m^{-3}		n_D	
		Experimental	Literature	Experimental	Literature
1,4 butanediol	303.15	1.0094	1.00967[24]	1.4470	-
	308.15	1.0068	1.00670[24]	1.4449	-
	313.15	1.0038	1.00373[24]	1.4430	-
	318.15	1.0004	1.00076[24]	1.4410	-
α-picoline	303.15	0.9352	0.9351[25]	1.4960	-
	308.15	0.9303	0.9304[25]	1.4941	-
	313.15	0.9257	0.9271[26]	1.4921	-
	318.15	0.9209	-	1.4899	-
β-picoline	303.15	0.9474	0.9474[25]	1.5003	-
	308.15	0.9427	0.9428[25]	1.4979	-
	313.15	0.9381	-	1.4956	-
	318.15	0.9345	-	1.4936	-
γ-picoline	303.15	0.9459	0.9454[25]	1.4998	-
	308.15	0.9406	0.9408[25]	1.4978	-
	313.15	0.9342	-	1.4957	-
	318.15	0.9296	-	1.4932	-

© 2016, IJSRCS All Rights Reserved

Starting from the R data, it is possible to study the related deviaiton ΔR, obtained by applying the relation (12). ΔR gives the strength of interaction in mixture and is sensitive function of wavelength, temperature and mixture composition.The results of this analysis are plotted in Figure-3 (a to c) for the three systems at various temperatures. The deviations from linearity of ΔR are similar for the three systems. Decreasing ΔR values are observed for increase in temperature. This decrease is less in case of 1,4-BD + γ-picoline system when compared to other two sytems.

Table-3: Densities, ρ, and refractive indices, n_D, as a function of mole fraction 1,4-BD at T= (303.15 – 318.15)K at atmospheric pressure 0.1MPa

x_1	ρ/kg.m^{-3}	n_D	ρ/kg.m^{-3}	n_D	ρ/kg.m^{-3}	n_D	ρ/kg.m^{-3}	n_D
1,4 butanediol (1) + α-picoline (2)								
	T=303.15K		T=308.15K		T=313.15K		T=318.15K	
0.0000	935.2	1.4960	930.3	1.4941	925.7	1.4921	920.9	1.4899
0.1236	945.8	1.4900	941.4	1.4882	937.1	1.4864	932.5	1.4845
0.2410	955.5	1.4843	951.4	1.4826	947.4	1.4809	943.1	1.4792
0.3524	964.3	1.4788	960.5	1.4772	956.8	1.4755	952.6	1.4740
0.4585	972.4	1.4735	968.9	1.4719	965.3	1.4702	961.3	1.4688
0.5594	979.8	1.4683	976.5	1.4667	973.1	1.4650	969.2	1.4637
0.6557	986.7	1.4632	983.6	1.4615	980.2	1.4598	976.5	1.4586
0.7477	993.1	1.4581	990.1	1.4563	986.8	1.4546	983.3	1.4535
0.8355	998.9	1.4531	996.1	1.4512	993.0	1.4495	989.5	1.4483
0.9195	1004.3	1.4482	1001.6	1.4462	998.6	1.4443	995.1	1.4431
1.0000	1009.4	1.4435	1006.8	1.4413	1003.8	1.4393	1000.4	1.4379
1,4 butanediol (1) + β-picoline (2)								
0.0000	947.4	1.5003	942.7	1.4979	938.1	1.4956	934.5	1.4936
0.1224	956.0	1.4939	951.6	1.4917	947.3	1.4896	943.9	1.4878
0.2389	963.9	1.4880	959.8	1.4859	955.8	1.4839	952.4	1.4822
0.3498	971.2	1.4822	967.4	1.4802	963.5	1.4783	960.2	1.4767
0.4556	977.9	1.4765	974.4	1.4745	970.7	1.4726	967.4	1.4711
0.5566	984.2	1.4708	980.9	1.4688	977.3	1.4669	974.1	1.4655
0.6531	989.9	1.4650	986.8	1.4630	983.4	1.4612	980.2	1.4598
0.7455	995.3	1.4593	992.3	1.4573	989.1	1.4555	985.8	1.4542
0.8339	1000.3	1.4538	997.5	1.4518	994.3	1.4499	991.0	1.4486
0.9187	1005.0	1.4485	1002.3	1.4464	999.2	1.4445	995.8	1.4432
1.0000	1009.4	1.4435	1006.8	1.4413	1003.8	1.4393	1000.4	1.4379
1,4 butanediol (1) + γ-picoline (2)								
0.0000	945.9	1.4998	940.6	1.4978	934.2	1.4957	929.6	1.4932
0.1224	954.6	1.4933	949.7	1.4914	943.8	1.4894	939.4	1.4872
0.2389	962.5	1.4872	958.1	1.4853	952.7	1.4835	948.5	1.4814
0.3498	969.9	1.4813	965.8	1.4794	960.8	1.4777	956.7	1.4757
0.4556	976.7	1.4755	972.9	1.4737	968.3	1.4719	964.4	1.4701
0.5566	983.1	1.4699	979.5	1.4681	975.3	1.4663	971.5	1.4646
0.6531	989.1	1.4645	985.7	1.4626	981.8	1.4608	978.1	1.4592
0.7455	994.7	1.4592	991.5	1.4572	987.9	1.4554	984.3	1.4539
0.8339	999.9	1.4539	997.0	1.4519	993.6	1.4500	990.1	1.4486
0.9187	1004.8	1.4487	1002.0	1.4465	998.8	1.4446	995.4	1.4432
1.0000	1009.4	1.4435	1006.8	1.4413	1003.8	1.4393	1000.4	1.4379

© 2016, IJSRCS All Rights Reserved

Table- 4: Coefficients A_i of equation (12) along with standard deviations σ of binary mixture properties.

Parameter	T/K	a	b	c	d	e	σ
1,4 butanediol + α-picoline							
Δn_D	303.15	6.54E-03	2.15E-03	-2.25E-03	-1.53E-03	9.49E-04	1.27E-05
	308.15	8.37E-03	2.58E-03	-1.99E-03	-1.42E-03	-2.68E-04	9.60E-06
	313.15	9.55E-03	2.55E-03	-9.44E-05	-1.28E-03	-1.38E-03	8.91E-06
	318.15	1.13E-02	3.02E-03	2.02E-03	-3.51E-04	-2.68E-03	1.66E-05
ΔR	303.15	-4.81E-02	1.82E-02	-1.52E-02	-8.38E-03	8.63E-03	7.28E-05
	308.15	-4.44E-02	2.10E-02	-1.34E-02	-7.38E-03	2.57E-04	4.86E-05
	313.15	-4.31E-02	2.13E-02	-3.26E-03	-5.90E-03	-6.96E-03	4.53E-05
	318.15	-3.82E-02	2.44E-02	3.67E-03	-2.42E-03	-8.70E-03	8.47E-05
1,4 butanediol + β-picoline							
Δn_D	303.15	8.38E-03	3.19E-04	-6.13E-03	2.14E-05	1.61E-03	1.13E-05
	308.15	9.59E-03	1.65E-04	-5.79E-03	7.04E-05	2.06E-03	4.80E-06
	313.15	1.08E-02	1.17E-04	-4.56E-03	2.32E-04	9.61E-04	7.84E-06
	318.15	1.16E-02	4.05E-04	-3.61E-03	-1.62E-05	7.10E-04	1.12E-05
ΔR	303.15	2.12E-02	4.88E-03	-2.59E-02	1.16E-03	5.04E-03	3.09E-05
	308.15	-1.95E-02	4.58E-03	-2.38E-02	1.77E-03	6.33E-03	2.10E-05
	313.15	-1.75E-02	4.29E-03	-1.99E-02	3.75E-03	3.20E-03	3.20E-05
	318.15	-1.54E-02	5.75E-03	-1.44E-02	4.39E-03	1.33E-03	4.87E-05
1,4 butanediol + γ-picoline							
Δn_D	303.15	5.69E-03	2.39E-03	1.63E-03	7.05E-04	-2.78E-03	1.05E-05
	308.15	6.62E-03	2.07E-03	1.90E-03	1.38E-03	-3.63E-03	1.06E-05
	313.15	7.83E-03	1.91E-03	1.86E-03	1.26E-03	-3.08E-03	1.12E-05
	318.15	8.57E-03	2.11E-03	1.97E-03	5.40E-04	-1.72E-03	1.28E-05
ΔR	303.15	-3.08E-02	1.56E-02	4.64E-03	3.51E-03	-1.14E-02	4.38E-05
	308.15	-3.10E-02	1.47E-02	6.12E-03	6.67E-03	-1.69E-02	4.35E-05
	313.15	-3.11E-02	1.49E-02	5.58E-03	5.96E-03	-1.40E-02	4.04E-05
	318.15	-3.00E-02	1.64E-02	6.10E-03	1.60E-03	-9.00E-03	2.69E-05

Table- 5: Calculated APD for different "Mixing rules" applied to the selected binary systems at T = 303.15 to 318.15 K.

T / K	A-B	E	E-J	G-D	H	L-L	N	Os	W
	1,4-BD + α-picoline								
303.15	0.040	0.0409	0.031	0.045	0.0512	0.0516	0.0635	0.0695	0.0444
308.15	0.059	0.0592	0.049	0.064	0.0696	0.0701	0.0822	0.0882	0.0628
313.15	0.074	0.0742	0.064	0.079	0.0846	0.0850	0.0972	0.1032	0.0777
318.15	0.095	0.0958	0.086	0.100	0.1058	0.1063	0.1181	0.1240	0.0992
	1,4-BD + β-picoline								
303.15	0.028	0.0280	0.016	0.033	0.0400	0.0407	0.0544	0.0614	0.0321
308.15	0.041	0.0415	0.030	0.047	0.0534	0.0541	0.0678	0.0747	0.0456
313.15	0.055	0.0553	0.044	0.060	0.0671	0.0679	0.0814	0.0883	0.0593
318.15	0.066	0.0661	0.055	0.071	0.0777	0.0784	0.0917	0.0985	0.0701
	1,4-BD + γ-picoline								
303.15	0.003	0.0034	0.007	0.008	0.0153	0.0160	0.0295	0.0363	0.0075
308.15	0.012	0.0125	0.001	0.018	0.0244	0.0252	0.0388	0.0457	0.0166
313.15	0.025	0.0253	0.014	0.030	0.0372	0.0380	0.0516	0.0585	0.0294
318.15	0.035	0.0351	0.024	0.530	0.0466	0.0473	0.0604	0.0671	0.0391

© 2016, IJSRCS All Rights Reserved

The deviations of theoretical values from experimental ones are temperature-independent. This may be attributed to the fact that variation in refractive index with temperature is compensated by the change in density of the liquid mixture. However, in cases where the variation is significant with change in temperature, it can be used for interpreting the structure and interactions in the liquid by computing other dielectric, optical and acoustical properties using experimental data. If the concept of excess volume (which is an indirect measure of interaction) is taken into consideration in various mixing rules, the deviation between the observed and theoretical values of refractive index may be reduced.

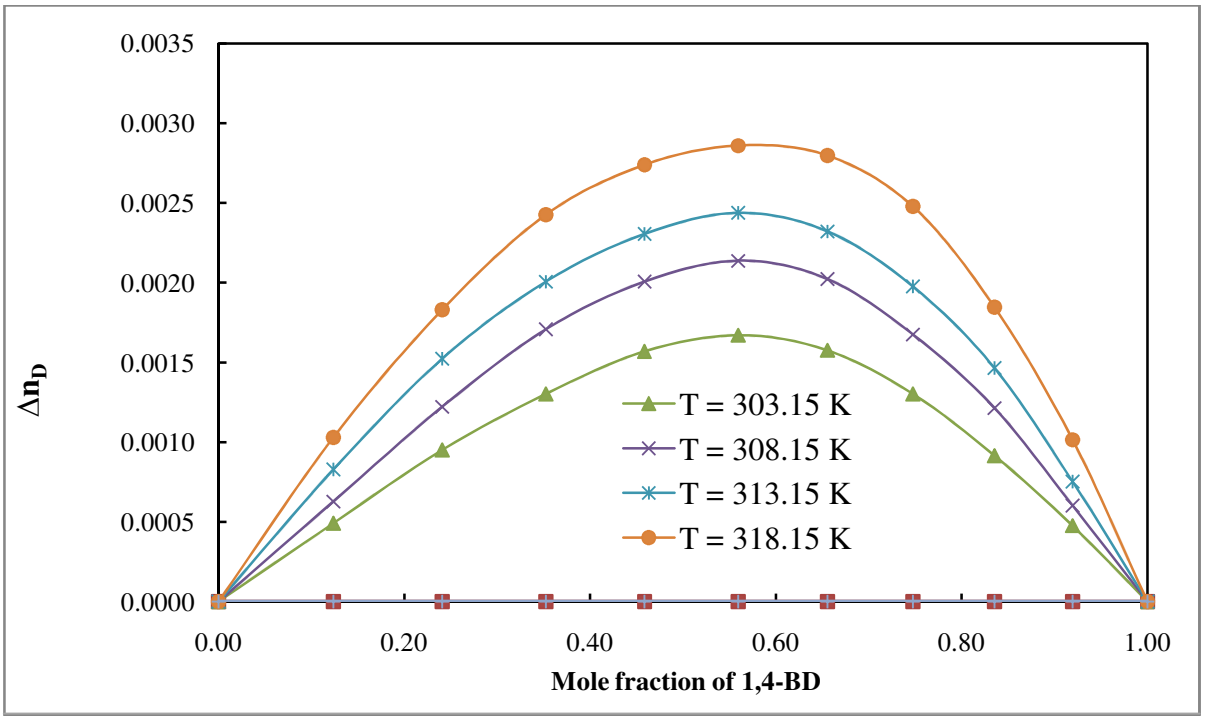

Figure 1(a): Plots of deviation in refractive index, Δn_D against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + α-picoline.

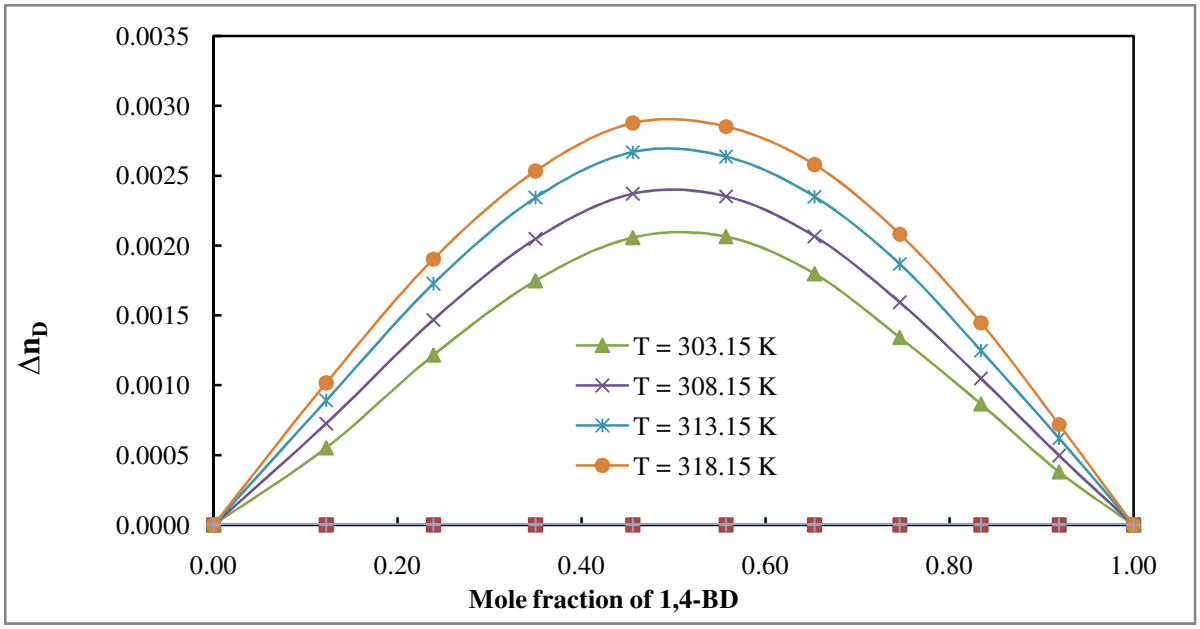

Figure 1(b) Plots of deviation in refractive index, Δn_D against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + β-picoline.

© 2016, IJSRCS All Rights Reserved

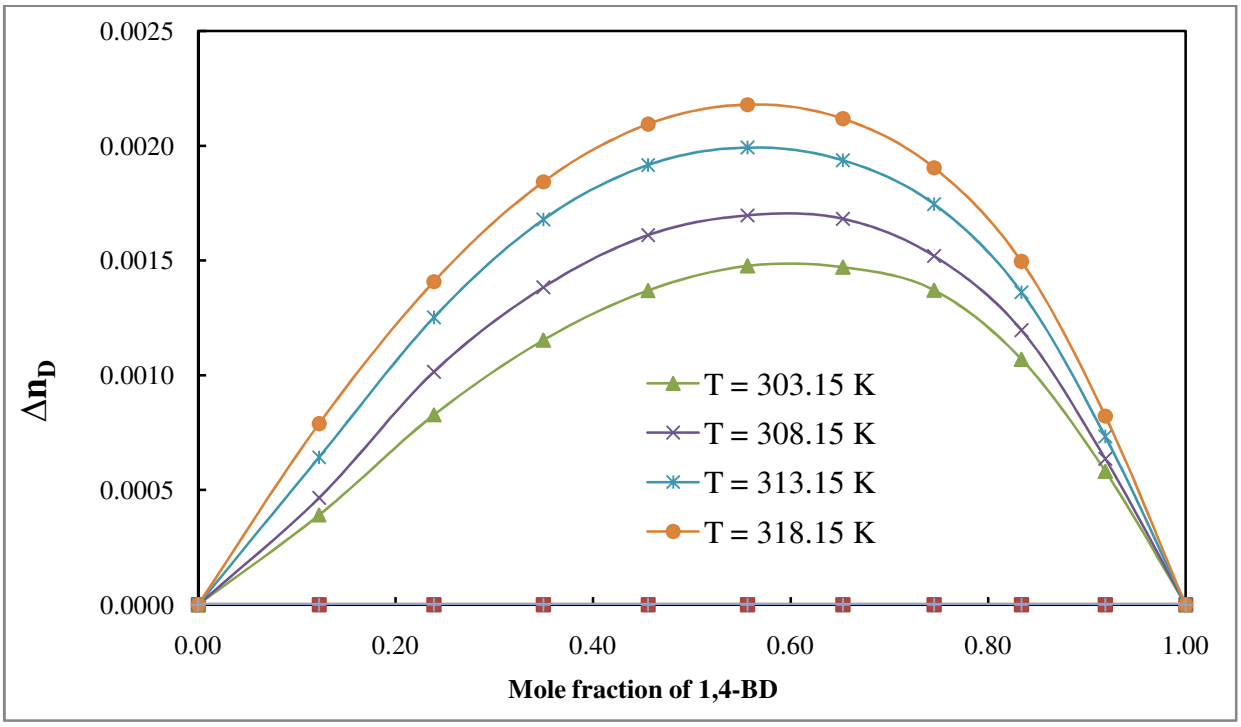

Figure 1(c): Plots of deviation in refractive index, Δn_D against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + γ-picoline.

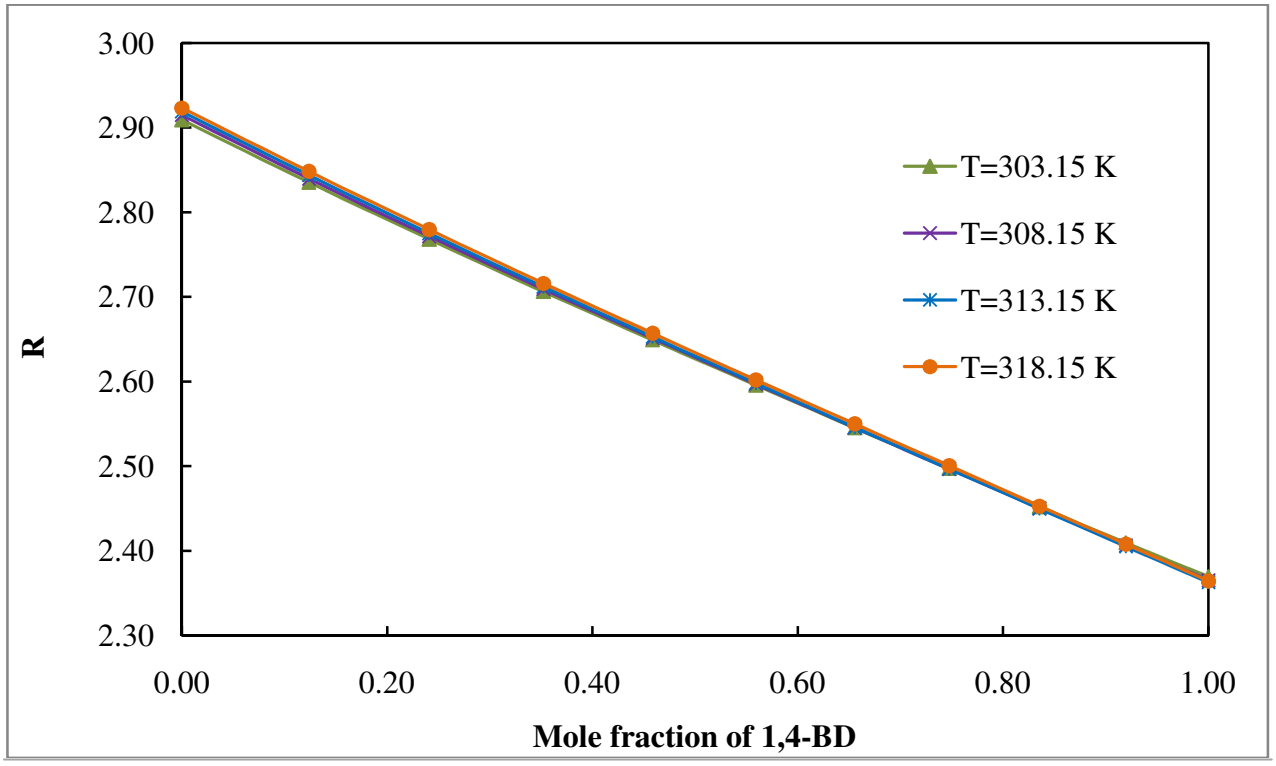

Figure 2(a): Plots of molar refraction, R against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + α-picoline.

© 2016, IJSRCS All Rights Reserved

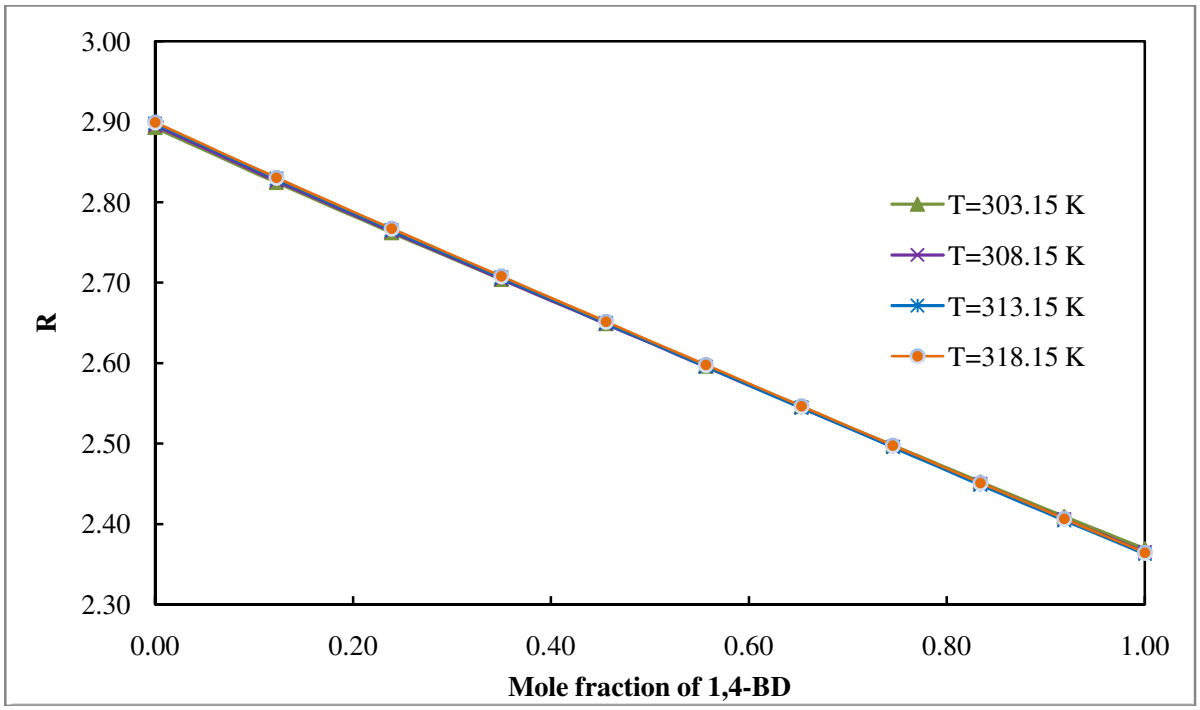

Figure 2(b): Plots of molar refraction, R against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + β-picoline.

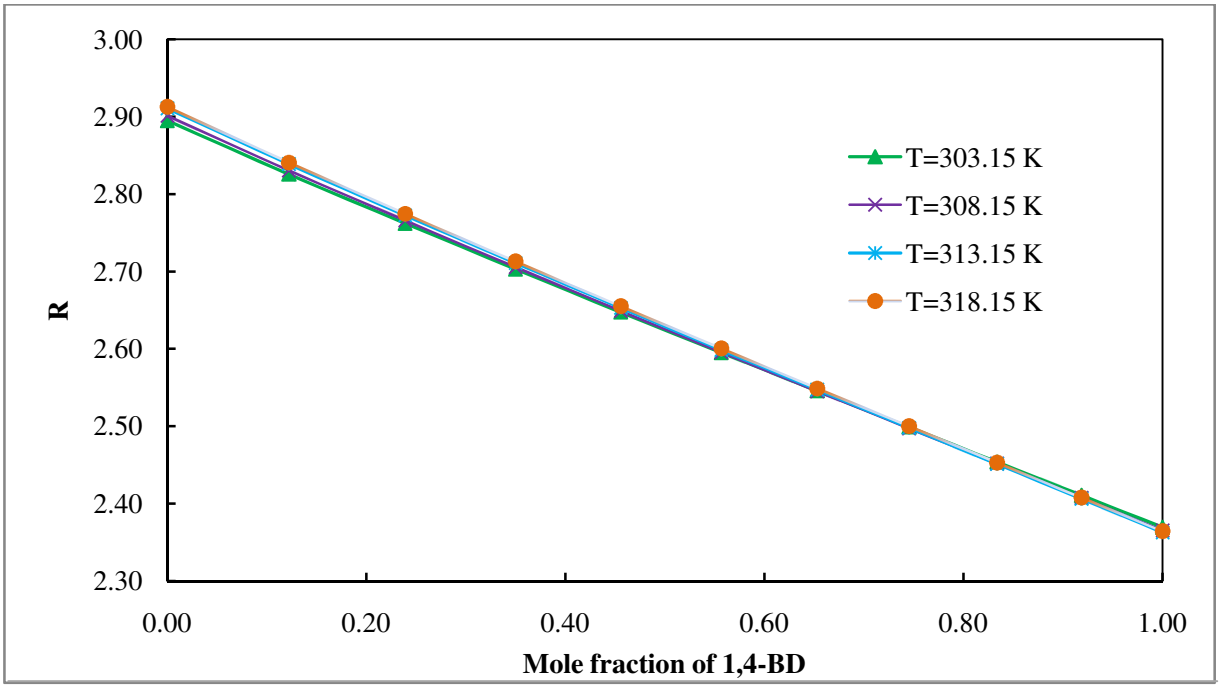

Figure 2(c): Plots of molar refraction, R against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + γ-picoline.

© 2016, IJSRCS All Rights Reserved

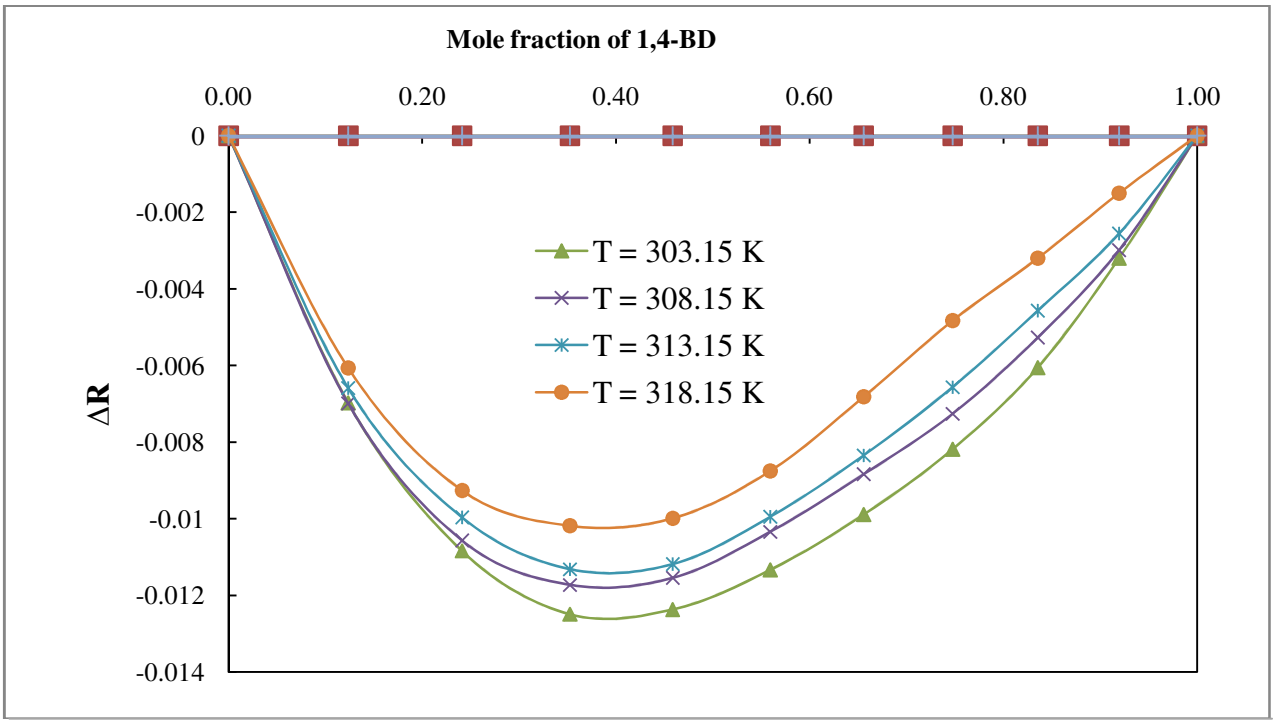

Figure 3(a): Plots of deviation in molar refraction, **ΔR** against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + α-picoline.

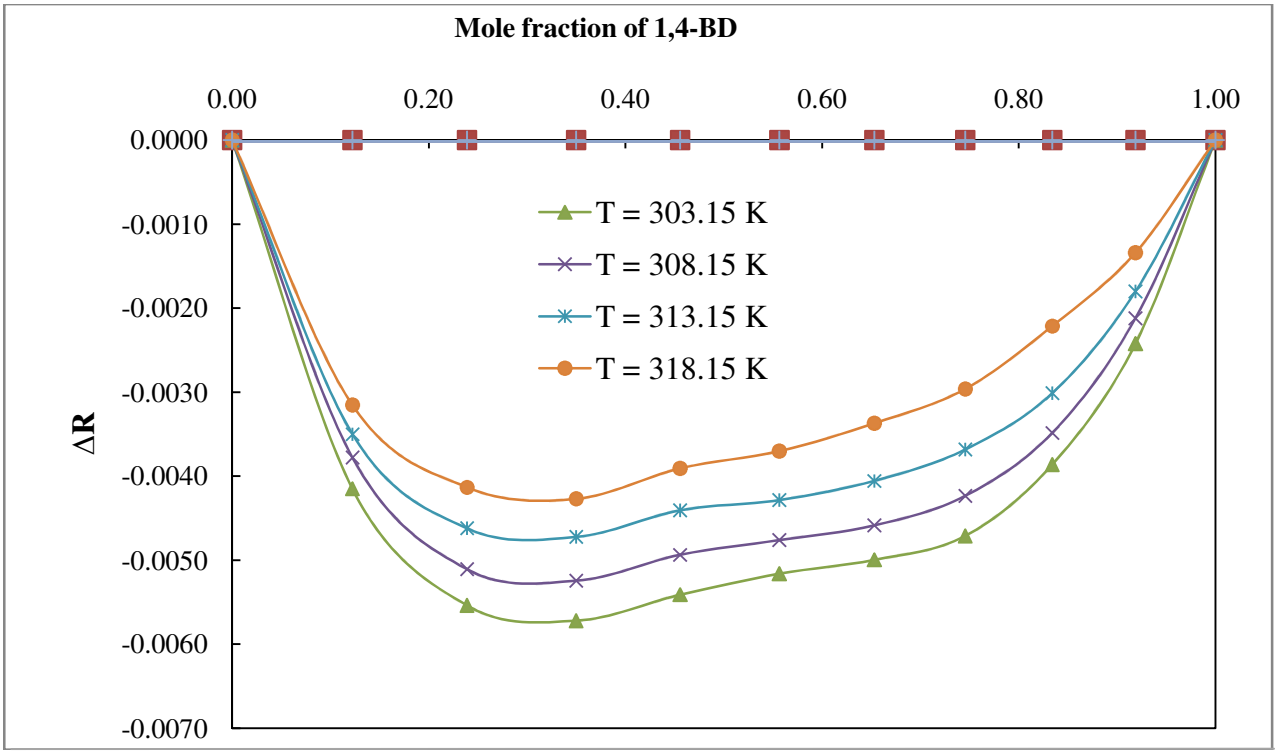

Figure 3(b): Plots of deviation in molar refraction, **ΔR** against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + β-picoline.

© 2016, IJSRCS All Rights Reserved

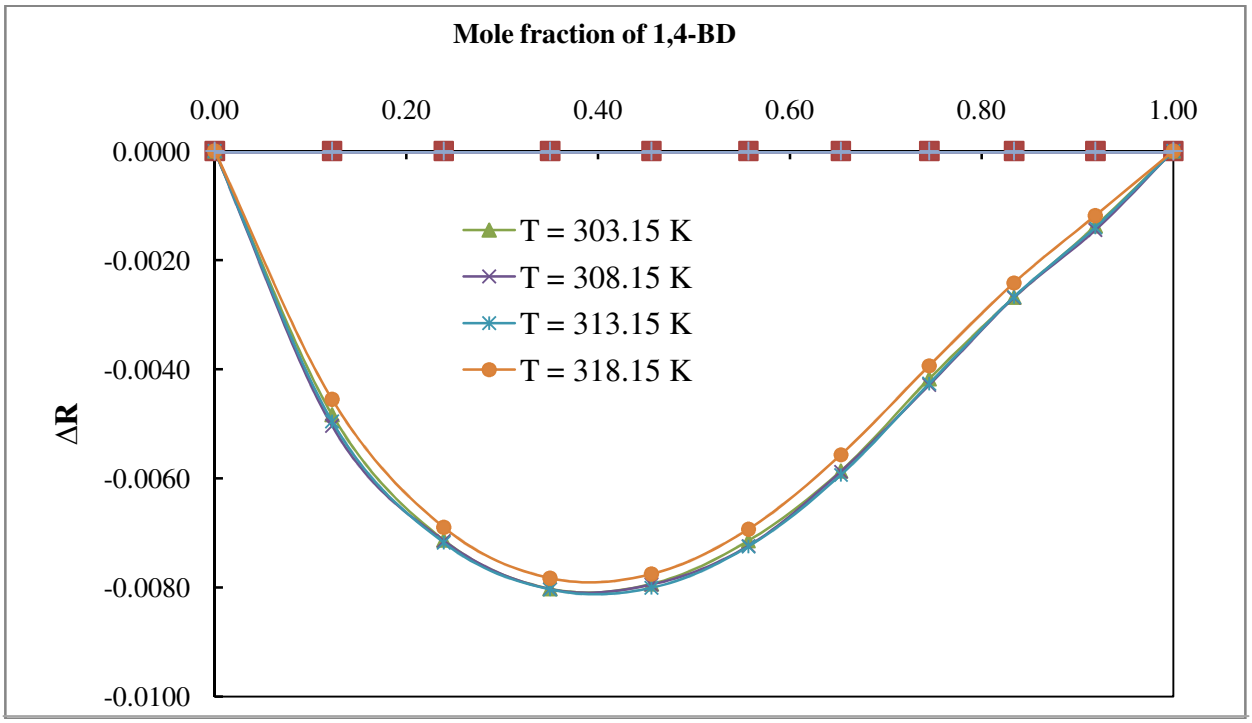

Figure 3(c): Plots of deviation in molar refraction, **ΔR** against mole fraction x_1 of 1,4-BD at T = (303.15-318.15) K for 1,4-BD + γ-picoline.

V.CONCLUSION

Density and refractive index values are measured experimentally and various mixing rules of refractive index were used to test their validity for binary mixtures. It may be concluded that all the mixing rules discussed are interrelated in a simple quantitative manner and perform well within the limits of experimental error. Negative and positive deviations are observed between experimental and theoretical values calculated by using various theories/models. The lowest deviations for the calculated refractive indices have been obtained by using Eyring-John equation, whereas the Oster equation gives the highest deviations at all temperatures for all the mixtures studied. Deviations in refractive index and molar refraction are observed to be positive and negative respectively for all the three systems and for all the temperatures studied.

REFERENCES

[1] S GovardhanRao, T Madhu Mohan, T Vijaya Krishna, K Narendra, and B. SubbaRao. "Thermophysical properties of 1-butyl-3-methylimidazolium tetrafluoroborate and N-methyl-2-pyrrolidinone as a function of temperature",J. Mol. Liq., Vol-**211**, Page No (**1009-1017**), **November 2015**.

[2] Edward Zorebski and Monika Geppert-Rybczynska. "Thermodynamic and transport properties of (1-butanol + 1,4-butanediol) at temperatures from (298.15 to 318.15)K",J. Chem. Thermodyn. Vol-**42**, Page No (**409-418**), **March 2010**.

[3] A K Nain. "Refractive indices and deviations in refractive indices for binary mixtures of formamide with 1-butanol, 2-butanol, 1,3-butanediol, and 1,4-butanediol at temperatures from 293.15 to 318.15 K", J. Chem. Eng. Data, Vol-**53**, Issue-**5**, Page No (**1208-1210**), **April 2008**.

[4] Mandeep Singh Bakshi."Thermodynamic behaviour of mixtures. Part 2.—Mixtures of acetonitrile with β-picoline, γ-picoline, 2,6-lutidine, isoquinoline and benzene at 25 °C", J. Chem. Soc. Faraday Trans. Vol-**89**,Issue -**16**, Page No(**3049-3054**), **1993**.

[5] W Martindale, The Extra Pharmacopoeia, Pharmaceutical Press, London, **1989**.

[6] J V Srinivasu, K Narendra, T S Krishna, B SubbaRao. "Study of volumetric and thermodynamic properties of binary mixtures 1,4-butanediol with methylpyridine isomers at different temperatures",J. Mol. Liq.,Vol-**216**, Page No(**455-465**), **April 2016**.

[7] D F J Arago and J B Biot, Mem. Acad. Fr.,Vol-**7**, **1806**.

[8] J F Eykman, "Reflectometric Research", Rec. Trav. Chim., Vol-**14**, Page No(**185-202**), **1895**.

[9] H Eyring and M.S. John, Significant liquid structures, John Wiley, New York, **1969**.

[10] F Gladstone and D. Dale, "Researches on the refraction, dispersion and sensitiveness of liquids", Phil. Trans. Royal Soc., Vol-**153**, Page No (**317-343**), **1864**.

[11] W Heller, "Remarks on refractive index mixtures rules", J. Phys. Chem, Vol-**69**, Page No(**1123-1129**), **1965**.

© 2016, IJSRCS All Rights Reserved

[12] H A Lorentz, "About the relationship between the velocity of propagation of light of body density", Ann. Phys., Vol-**9**, Page No(**641-665**), **1880**.

[13] S S Kurtz and A L Ward,"The refractivity intercept and the specific refraction equation of Newton", J Franklin Inst., Vol-**222**, Page No(**563-569**), **1936**.

[14] G Oster, "The scattering of light and its applications to chemistry", Chem. Rev. Vol. **43**, Page No(**319-365**), **1948**.

[15] O Weiner, Leipz. Ber. Vol-**62**, Page No(**256-260**), **1910**.

[16] M C Saxena, Indian J Chem., Vol-**10**, Page No(**636-641**), **1998**.

[17] Herminio C, Sandra G.G., Luisa S, Oscar C, Carlos F, Eulogio J. "Densities, viscosities, and refractive indexes for $\{C_2H_5CO_2(CH_2)_2CH_3+C_6H_{13}OH+C_6H_6\}$ at T=308.15K", J. Chem. Thermodyn. Vol-**35**, Page No(**1129-1137**),**July2003**.

[18] K Narendra, P Narayana Murthy, ChSrinivasu, "Refractive indices of binary liquid mixtures at different temperatures", Asian J Appl. Sciences,Vol-**4**, issue-**5**, Page No(**535-541**), **2011**.

[19] B Sudhamsa, M SarathBabu and K Narendra. "Application of refractive index mixing rules to binary system", Journal of applicable Chemistry, Vol-**3**, Issue-**3**, Page No(**1272-1276**),**March2014**.

[20] M Srilakshmi, K Narendra, ChKavitha, ASarathBabu, ARatnakar. "Refractive Properties for Binary Mixtures Containing DEC+o-xylene or m-xylene or p-xylene", Int. J. Innovative Research in Science Engineering and Technology, Vol-**4**, Issue-**12**, Page No(**12598-12612**), **December 2015**.

[21] A I Vogel. Text book of Practical Organic Chemistry, fifth ed. Longman Green, London, **1989**.

[22] J A Riddick, W B Bunger, T Sakano, Organic Solvents: Physical Properties and Methods of Purification, Wiley-Interscience, New York, **1986**.

[23] M V Ratnam, SudhirMohite, M Nandini. "Excess properties of diethyl carbonate + ketone binary mixtures at variable temepratures: Application of PFP theory to excess volume", J. Mol.Liq., Vol-**17**, Page No(**229-236**), **2013**.

[24] A K Nain, "Densities and volumetric properties of binary mixtures of formamide with 1-butanol, 2-butanol, 1,3-butanediol and 1,4-butanediol at temperatures between 293.15 and 318.15 K", J. Solution Chem. Vol-**36**, Page No(**497-516**), **2007**.

[25] SubhashSolanki, NeetiHooda, VK Sharma "Topological investigations of binary mixtures containing Ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate and pyridine or isomeric picolines" J. Chem. Thermodyn. Vol-**56**, Page No(**123-135**), **2013**.

[26] M J Lee, M C Wei, "Densities and viscosities of 2-butanone/dibutyl ether, 2-picoline/2-butanone and 2-picoline/water mixtures", J. Chem. Eng. Data. Vol-**37**, Page No(**209-212**), **1992**.

[27] O Redlich, AT Kister, "Algebraic representation of thermodynamic properties and classification of solutions", Ind. Eng. Chem. Vol-**40**, Page No(**345-348**), **1948**.

[28] A Pineiro, P Brocos, A Amigo, M Pintos, R. Bravo. "Prediction of excess volumes and excess surface tensions from the refractive indices", Phys. Chem. Liq., Vol-**38**, Page No(**251-260**), **2000**.

[29] P Brocos, APineiro, R Bravo, A Amigo. "Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations", Phys. Chem. Chem. Phys. Vol-**5**, Page No(**550-557**), **2003**.

AUTHORS PROFILE

Mr.J.V.Srinivasuisworking as an assistant professor in the Basic Science department, Shri Vishnu Engineering college for women, Bhimavaram. He has 7 years of teaching experience and 4 years of research experience .

Dr. K Narendra, working as assistant professor in departmnet of Physics, V.R. Siddhartha Engineering College since 2004. He has a teaching experience of 18 years. He published 76 papers in various National and International journals. He is the author of 3 books. He presented 17 papers in various National and International conferences/workshops.

Dr.B.Subbarao working as Reader in the Department of Physics, V.S.R&N.V.R college Tenali.He has 20 years of teaching experience.He published 75 papers in various Inter nationaljournals.He presented 20 papers in various National and International conferences.He guided 4 candidates for Ph.D' and 7 candidates forM.Phill degrees. Heis guiding 4 Ph.Dstudents.His areas of interest are Luminescence and Ultrasonic's.

© 2016, IJSRCS All Rights Reserved